No. 100. Vol. 18.

THE JOURNAL OF THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

The publication of number One Hundred of the Journal of the Institution of Petroleum Technologists merits some reference to its history.

The first number was published in June, 1914, and the first six volumes were issued in four quarterly parts. Volumes Seven and Eight were each made up of five parts, and from then until Volume Fifteen (1929) six bi-monthly parts were published to each volume, with an additional number in 1924 to contain the papers read at the First Empire Mining and Metallurgical Congress. In 1930, nine parts were issued, and last year the long-sought-for ideal of a monthly journal was attained.

The total number of pages in Volume One was 324, while the last Volume (Seventeen) was one of 1330 pages. Of these pages, 760 were occupied by papers read before the Institution and by articles specially contributed, the remaining 570 being taken up by Abstracts of current technical literature and Patent Specifications.

The section of the Journal devoted to Abstracts is one of increasing importance, particularly when difficulties of time and space make impossible the reading of the multiplicity of technical journals. Readers are thus able to make a critical selection of the more important articles to be read at leisure. The Abstracting Staff are to be congratulated on the success of their efforts to produce readable and accurate summaries of original work from journals in the United Kingdom and abroad.

In its inception, the Journal was fortunate in having as Honorary Editor the late Mr. W. H. Dalton, and in one of his well-known editorials he wrote, " . . . matter published in the Journal is as seed scattered on the wind, to germinate or not as chance may befall." That the seed is scattered is well evidenced by the Journal's geographic distribution, embracing practically every country in the world, and a perusal of the list of those who regularly receive it gives good cause for anticipating that the percentage of germination is high.

The success of the Journal is in no small part due to the voluntary efforts and the enthusiasm of the Publication Committee, so ably guided by Dr. A. E. Dunstan. Members of this Committee are very active in their endeavours to maintain the high standing of the Journal.

J. KEWLEY, *President.*

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

THE ONE HUNDRED AND FORTIETH GENERAL MEETING of the Institution of Petroleum Technologists was held at the House of the Royal Society of Arts, John Street, Adelphi, on Tuesday, January 12th, 1932, the Chair being taken by Mr. J. McConnell Sanders, F.I.C., F.C.S., Member of Council.

The Secretary read the list of candidates nominated for election and the following list of members elected :—

As Members.—George Clifford Carr, Frederick Arthur Couse, Douglas Alexander Fell, Lester Raymond Gray, Raymond Clyde Rich.

As Associate Members.—Alan John Cresswell, Henry Thomas John Martin, Cecil Hugh Le May, Robert Lewis Speer.

As Transference to Associate Members.—Charles Frederick Carre Moore.

As Associate.—Herbert James Dykes.

The following paper was then read:—

The Chemistry of the Conversion of Algæ into Bitumen and Petroleum and of the Fucosite-Petroleum Cycle.

By J. E. HACKFORD, B.Sc., F.I.C. (Member).

INTRODUCTION.

AMONG the several theories at present existent as to the origin of petroleum oils, one of general acceptance is that some types of petroleum have been derived from the decomposition of marine vegetation ; but the mechanism of the chemical reactions involved in this metamorphosis have not hitherto been fully investigated.

No facts supporting the suggestion that oils are produced by the natural decomposition of algæ have yet been brought to light, nor indeed, has oil been produced from algæ in a manner in any way similar to processes, or under conditions resembling, those obtaining in nature.

The author has been able to establish :—

(1) The formation of oil from algæ by processes similar to those obtaining in nature.

(2) The presence of the decomposition products of algæ in both naturally occurring oils as obtained from wells, and also from seepage oils and bituminous deposits.

(3) The reconversion of oils, various oil seepages, and some seepage products into bodies closely resembling, and in some instances identical with the constituents and decomposition products of algæ.

(4) The formation of oils and bitumens from sugars.

(5) The reconversion of oils into bodies resembling bitumens, which upon hydrolysis yield sugars.

While the above work supports the algal theory of the origin of some classes of petroleum, the data obtained shows that oil and bitumen are in the main produced from the sugars resultant upon the hydrolysis of algæ.

On this account it may be advisable to rename the vegetal theory, and to call it "The Carbohydrate Theory of the Origin of Oil."

Definitions.

The term "Protobitumen," as employed herein, is a chemical definition, and must not be confused with the commercial definition as accepted by the International Committee for the Standardisation of Nomenclature and Tests of Road Materials, and by the American Society for Testing Materials. This reads :—

"*Bitumens*.—Mixtures of hydrocarbons of natural or pyrogenous origin or combinations of both (frequently accompanied by their non-metallic derivatives) which can be gaseous, liquid, semi-solid or solid, and which are completely soluble in carbon disulphide."

Protobitumen is a partially reduced* carbohydrate which, upon further or total reduction, yields oil. Conversely, protobitumen is a partially reduced carbohydrate formed by the oxidation of oil. Naturally occurring protobitumens may contain other decomposition products of algæ, such as metallic salts and organic derivatives of sulphur and nitrogen, according to the type of the parent algæ.

It is possible, and indeed probable, that the chemical definition of protobitumen as given above will be found to apply also to bitumens, which may have been derived from other sources. In the meantime, however, it is limited to the bituminous material derived from algæ, and to the oxidised products of the oils obtained from them. This procedure is adopted because there is at present no real chemical evidence to justify oils and bitumens of animal or other origins being included.

* By *reduction* is understood the treatment of a substance in such wise that the percentage of hydrogen in the end product is greater than that in the original compound.

Oil.—The term oil as used herein denotes a mixture of hydrocarbon oils, and such alcohols, ketones, aldehydes, carboxylic and poly-hydroxy-carboxylic acids which yield hydrocarbons upon reduction. These latter compounds are found in some of the well oils and seepage oils herein discussed.

Asphaltenes.—That portion of bitumen which is soluble in carbon disulphide, but insoluble in ethyl ether.

Kerotenes.—That portion of bitumen or protobitumen which is insoluble in carbon disulphide.

Kerols.—That portion of the kerotenes which is soluble in both chloroform and pyridine.

Keroles.—That portion of the kerotenes which is soluble in pyridine, but insoluble in chloroform.

Kerenes.—That portion of the kerotenes which is insoluble in organic solvents.

Kerites.—Naturally occurring bitumens and protobitumens composed appreciably or wholly of kerotenes.

Algarose is chemically pure protobitumen prepared by the acid hydrolysis of sugars. It reduces Fehling solution, and is free from metallic salts and organic derivatives of sulphur and nitrogen.

Algarites are naturally occurring protobitumens, composed chiefly of algarose, together with the metallic salts, sulphur, and the nitrogenous organic derivatives simultaneously formed during the acid hydrolysis of algæ.

It occurs in nature as a natural bitumen, or highly bituminous shale in the form of McKittrite, and is capable of yielding oil by reduction.

Fucose is the sugar obtained by hydrolising the polymer fucosan, which is a component of the cell wall of marine algæ.*

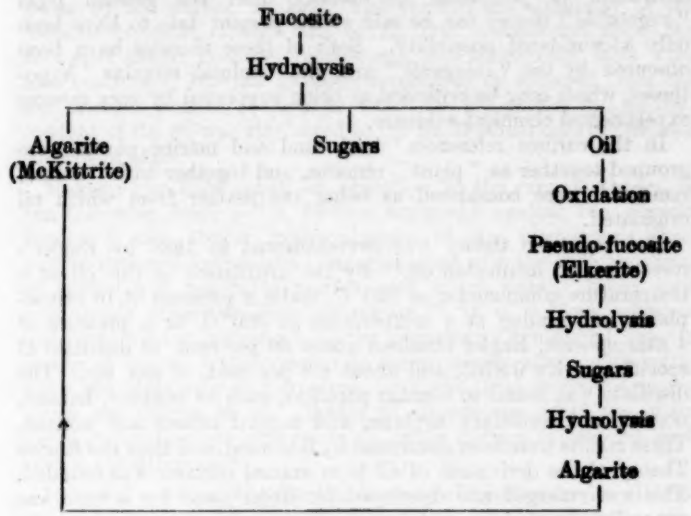
Fucosite is a naturally occurring mineral, which is composed of the lesser water-soluble portions of seaweed. The structure has almost been entirely lost by the action of bacteria and oxygen. It has been called "Fucosite" because it contains a sugar complex which is liberated by either alkaline or acid hydrolysis. During the latter process oil and algarose are formed. In the samples hereinafter quoted the fucosite mainly consists of a fucose pentosan.

Elkerite and pseudo-fucosites.—Elkerite is a naturally occurring bitumen formed by the slow oxidation of oil. It is a fucose pentosan—hence the class term "pseudo-fucosite" to distinguish it from the seaweed complex, Fucosite. It is built up from oil, cf. algarite, which is a decomposition product of algæ.

* "Dictionary of Applied Chemistry," Thorpe, 1912, vol. I., p. 644.

The Fucosites or the Sugar-Forming Bitumens.

The following diagram illustrates the inter-relationship between the various types of sugar-forming bitumens :—



Fucosite	Hydrolysis →	Algarite
Oil	Oxidation →	Pseudo-fucosite (Elkerite)
Pseudo-fucosite	Hydrolysis →	Sugars
Pure sugars	Hydrolysis →	Algarose
Impure sugars ex fucosite	Hydrolysis →	Algarite

Section I.

The Formation of Oil by the Natural Decomposition of Algæ.

The development of the Algal theory.—The Algal theory of the derivation of petroleum as distinct from the general term "vegetable" theory can be said at the present date to have been only a considered possibility. Both of these theories have been obscured by the "inorganic" and the "animal remains" hypotheses, which may be criticised as being supported by very meagre experimental chemical evidence.

In the earliest references,[1] both land and marine plants were grouped together as "plant" remains, and together with "animal remains" were considered as being the matter from which oil originated.

The vegetable theory was overshadowed in 1888 by Engler's researches on menhaden oil.[2] By the distillation of this oil at a temperature commencing at 320° C. under a pressure of 10 atmospheres and ending at a temperature of 400° C. at a pressure of 4 atmospheres, Engler obtained about 60 per cent. of distillate of specific gravity 0.8105, and about 8.9 per cent. of gas, etc. The distillate was found to contain paraffins, such as pentane, hexane, normal and secondary heptane, and normal octane and nonane. These results were later confirmed by Redwood, and thus the Engler Theory of the derivation of oil from animal remains was founded. This was enlarged and developed by Höfer[3], and for a time was generally accepted.

It was not long, however, before doubts began to arise as to the universal applicability of this theory, and in particular Orton,[4] upon the basis of his observations made in 1886, insisted that the production of oil must have occurred in nature at temperatures below 200° C.

In 1894 Porter[5] pointed out that the gases obtained during the distillation of menhaden oil by Engler differed from naturally occurring petroleum gases, inasmuch as they contained 25-38 per cent. of carbon monoxide and a considerable proportion of olefines, while the percentage of saturated paraffinic gases was small. Porter then pointed out that, by the natural decomposition of marine vegetation under water, *i.e.*, at low temperatures, gases are evolved similar in composition to natural gases.

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[1] Henkel, 1725.

[2] *Ber. deut. chem. Gesellschaft*, 1888, **21**, 1816; 1889, **22**, 592. See also Engler and Seidner, *Dinglers polytech. Jour.*, 1889, **271**, 515.

[3] Höfer, "Das Erdol," p. 118.

[4] Orton, "Prelim. Report on Petrol. and Imflamm. Gas," 1886, p. 11.

[5] Porter, *Am. Chem. Jour.*, 1894, **16**, 406.

Founded on this piece of direct evidence, Porter supports the marine vegetation theory ; and in the same year Witt[6] showed that the waxy matter secreted by diatoms may contribute to the production of petroleum.

Confirmatory evidence of the production of oil from algæ was given by the author[7] in 1922, who showed the similarity of the metallic contents of algæ and of oil, and commented upon the fact that iodine, bromine, phosphorus, and ammonium salts were also common. The low nitrogen content of oil followed from the low nitrogen content of the algæ, whilst the low phenol and furfural content of the oil was attributed to the small percentage of cellulose present in algæ.

Ramsay[8] in 1924 raised an objection to the organic theory in the following form :—" A further argument against the organic theory is the almost entire absence of the nitrogenous and oxygenated compounds which are associated with the decomposition of animal and vegetable matter, and which usually break into compounds dissimilar from petroleum." It is dubious whether this objection can be upheld, as the nitrogenous content of organic matter is largely transformed into water-soluble ammonium salts, while the remainder is converted, *inter alia*, into tertiary amines, which are soluble in oil. Traces of ammonium salts[9] are often found in conjunction with crude oil, while tertiary amines are well known constituents.[10]

It is also questionable whether Ramsey's objection to the almost entire absence of oxygenated compounds can be allowed. We know that the percentage of oxygen by weight would be small, and therefore difficult to determine accurately, and we also know that vegetation is deprived of its oxygen content by bacterial action, etc.

Taylor[11] proved the suggestion, first made by Radzisewski,[12] that organic matter under sodium clays was decomposed by anærobic bacterial action with the production of gases similar to naturally occurring petroleum gases. The demonstration of the decomposition of sugars under these conditions is of considerable importance, inasmuch as these constitute a considerable proportion

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[6] See Redwood, " Treatise on Petroleum," Vol. I., 4th ed., p. 359.
[7] Hackford, *J.I.P.T.*, 1922, **8**, 197.
[8] Ramsay, *J.I.P.T.*, 1924, **10**, 88.
[9] Mrazac, *Petr. Times*, 1922, **8**, 340 ; and Palmer, *Econ. Geol.*, 1922, **17**, 100.
[10] Mabery, *Econ. Geol.*, 1916, **11**, 521–527.
[11] Taylor, *J.I.P.T.*, 1928, **14**, 825–840.
[12] Radzisewski, *Arch. Pharm.*, 1878, **3**, 455–459.

of the decomposition products of marine vegetation. He further suggests that "all shales overlying oil-bearing strata have undergone base exchange and hydrolysis," and that the medium produced by hydrolysis favours the bacterial action under alkaline anærobic conditions, with the formation of gases similar in composition to natural gas."

Modern opinions endorse Taylor's views; Thrask[13] states that "anærobic bacteria, because of their tendency to decrease the nitrogen and oxygen of organic matter on which they feed, probably produce compounds more similar in composition to petroleum than the original organic matter that was deposited by the sediments. Their action, therefore, may facilitate the generation of petroleum by purely chemical means." Thayer, and also Brooks, generally confirm these views, but Hammer[13] states that: "bacteria, by removing oxygen and nitrogen from organic matter, form compounds more closely related to petroleum than the original organic material, thus presumably facilitating the generation of petroleum by purely chemical means." Aerobic micro-organisms in the sea water and the upper layers of the sediments may form amino and lower fatty acids from more complex organic material. Anærobic bacteria characterise all but the surface layers of the deposits, and remove oxygen, nitrogen, and sulphur from the organic matter in the sediments. Some anærobic bacteria form methane, *but none is known to generate hydrocarbons that characterise petroleum.*

In a contribution to a recent paper by D. White on the subject of "Time versus Temperature in Petroleum Generation," Thrask[13a] extends the conclusions based on Maier and Zimmerly's work on oil-shale, by giving data of his own researches on the effect of heat on modern organic muds. He gives quantitative figures of the amount of organic matter converted into bitumen at temperatures ranging from 280° to 339° C. He concludes that the heat due to blanketing in the earth's crust probably produces bitumen from the organic contents of the sediments, and suggests *that the formation of bitumen is perhaps an intermediate step in the generation of petroleum.*

The Chemical Properties of Algæ.—Algæ are plants which absorb their mineral constituents by their whole surface from the waters in which they live. The same species of algæ may, therefore, contain different metals dependent upon the nature of the waters in which they exist. Seaweeds show many pecularities not shared

[13] Thrask, Thayer, Brooks, Hammer; see 16th Annual Meeting of Amer. Assoc. of Petr. Geol., 1931.

[13a] Thrask, *Bull. Amer. Assoc. Petr. Geol.*, 1931, **15**, 83–84.

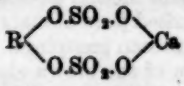
by terrestial plants. The presence of a multiplicity of elements in the mineral constituents, of ethereal sulphates in the cell wall constituents, the lesser amount of cellulose, the presence of alginic acid, the common occurrence of mannitol, the presence of obscure carbohydrates such as laminarin indicate a metabolism differing from that of the normal terrestial plant.

The predominating mineral is calcium, which exists in quantities of from 17 per cent. in *F. seratus* to 52 per cent. in the roots of *L. hyperboria* (calculated as calcium sulphate upon the dried material).

Many other metals and non-metals are present, and during this investigation several have been identified whose presence has not previously been recorded.

Calcium salts.—The calcium salts appear to be present partly as calcium sulphate and partly in organic combination.

Haas (1921)[14] found that *chondrus crispus* yielded an ash rich in calcium sulphate. even after prolonged dialysis, and assumed the existence of some form of masked sulphate such as an ethereal sulphate of the type represented by the formula



Chemical evidence for the correctness of this assumption was furnished by the fact that the masked sulphate could be converted into the ionised sulphate by hydrolysis. The ethereal sulphates are widely distributed, and have been identified in the following rhodophyceæ and phæophyceæ; *ceramium rubrum, delasseria sanguinea, delesseria alata, polysiphonia fastigiata, plumaria elegans, ascophyllum nodosum,* and *laminaria digitata.*

Neuberg and Ohle[15] in 1921 established the presence of the ethereal sulphate grouping in agar, the extract of a species of gelidium.

In the case of *chondrus,* the average molecular weight of the aqueous extract was 1000.[16] The proof of the existence of an ethereal sulphate depended on the fact that the percentage of sulphate contained in the hydrolysed solution of the hot extract was just twice that contained in the ash, from which it is clear that, of the two molecular proportions of suplhate here given, only the one combined with the calcium would be found in the ash, the other in the form of free sulphuric acid being lost during incineration.

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[14] Haas, *J. Biol. Chem.*,

[15] Neuberg and Ohle, *Biochem. Z.*, 125, p. 311.

[16] Haas and Wells, *J. Biol. Chem.*, 1923, 117, 698 et seq.

In the case of *ceramium rubrum* the following figures are given:—

Ash in crude weed	13·88 per cent.
SO_4 in above ash	15·63 „
SO_4 in weed by hydrolysis	4·13 „
SO_4 in weed by incineration	2·17 „

The following equation illustrates the reaction:—

$$R\begin{matrix}O{\cdot}SO_2{\cdot}O\\ O{\cdot}SO_2{\cdot}O\end{matrix}Ca + 2\,H_2O = R\begin{matrix}OH\\ OH\end{matrix} + CaSO_2 + H_2SO_4$$

Sodium, potassium, ammonium, and phosphorus ethereal salts have also been identified. Haas[16] states that evidence of phosphoric acid in organic combination has been obtained in the case of *chondrus*.

Bird and Haas[17] in 1931 made an attempt to elucidate the nature of the cell wall constituents of the laminariaceæ known as fucoidin and alginic acid. The former has been shown to be the calcium salt of a sulphuric ester of a non-reducing polymerised uronic acid complex combined with a methyl pentosan, since it yields on hydrolysis sulphate ions and methyl pentosan fucose.

Alginic acid is a polymerised form of manuronic acid and contains no pentosan or methyl-pentosan groupings. These facts emphasise the distinctive metabolism of the brown algæ, which appears to be founded upon a mannose, rather than a glucose basis—as is shown by the occurrence of mannitol and mannitan,[18] and the apparent absence of glucose in any appreciable amount. Hoagland and Lieb[19] state that in the carbohydrates of *macrocystis pyrifera* and *iridæa laminarioides* the acid precipitate complex known as "algin," yielded a pentazone closely resembling l-xylosazone. In the alcohol insoluble carbohydrate fraction (which are the salts of the calcium sulphonic esters) of macrocystis, a methyl pentose having the properties of fucose is present; a similar fraction from *iridæa* yielded only galactose.

Sugars.—Sugars other than the mannose and galactose mentioned have been identified among the hydrolytic products of decomposition of algæ. Bente, 1785, 1786, found levulinic acid, and also a sugar showing little or no optical activity in *chondrus crispus*. Hardicke, Bauer and Tollens (1867) established in carragen mucilage the presence of fructose and calculated that it contained 28 per cent. of galactose. They suggested that it might be present under the form of raffinose. Sebor (1900) confirmed the presence of fructose

[17] Bird and Haas, *J. Biol. Chem.*, 1931.
[18] Haas and Hill, *J. Biol. Chem.*, 1929.
[19] Hoagland and Lieb, *J. Biol. Chem.*, 1915, **23**, 287–297.

and glactose and showed small quantities of pentosan, and showed that raffinose was absent. He also found evidences of the presence of glucose. Wells[20] confirms the presence of pentosan.

Nitrogen Compounds.—Nitrogen exists in algæ to the extent of 1·485 per cent. in the case of *chondrus crispus*, and 4·65 per cent. in the case of *porphyralacinata*, both calculated on the dry matter.

Russel-Wells[21] showed that some of the nitrogen existed in the form of an ammonium ethereal salt of the type

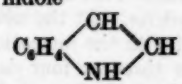
$$R.O.SO_2.ONH_4$$

Instances are given in the experimental section of this paper that tertiary amines and ammonium salts are formed upon acid hydrolysis.

Hoagland[22] states that of the total nitrogen of the kelps he examined, from one-third to one-fifth was soluble in water, and about the same proportion was found by Stutzer's method to be in the form of non-protein nitrogen.

Stewart[23] finds that the nitrogen of *nereocystis luetkeana* is readily converted into ammonia when mixed with soil, whilst that of *pelagophycus* is less readily changed. *Macrocystis pyrifera* changes very slowly in the soil, especially when it has been dried.

Lafar[24] states that indole



and Brieger, that B-methyl indole or skatole, together with phenol (Bauman), ortho-cresol and paracresol (Bauman and Brieger) are present in putrifying albuminoids. Leucine, lyrosine and valeric acid are also found.

$$\underset{\text{Leucine.}}{CH_3.CH_2.CH_2CH_2CH.NH_2.COOH} + 2\,H_2O$$

$$= \underset{\text{Iso Valeric acid.}}{(CH_3)_2CH.CH_2.COOH} + H_2O + CO_2 + NH_3$$

Cellulose.—It is thought that the cellulosic contents of algæ give rise upon decomposition to furfural and phenols, the presence of which have been noted by Haas.

Norman[25] states that there is definite evidence for the production of some intermediary substance which yields furfural. It is probable

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[20] *J. Biol. Chem.*, 1922, **16**, 584.
[21] *J. Biol. Chem.*, 1922, **16**.
[22] *J. Agric. Research*, 1915, **4**, 39–58.
[23] *J. Agric. Research*, 1915, **4**, 21–37.
[24] "Technical Mycology," Vol. I., p. 291.
[25] *J. Biol. Chem.*, 1929, **23**, p. 1384.

that this is produced transitionally in the degradation of cellulose, although there is scanty support for this theory.

Nearly all the iodine present in seaweed (Okuda and Etc[24]) is in organic combination. The greater part of it is in a form soluble in water, strong alcohol, dilute alkalis or acids. It is not a protein compound. Concentrated solutions of sulphuric acid and sodium hydroxide decompose it completely. Decomposition is also brought about by micro-organisms, but there is no enzyme in the plant to effect this.

It occurred to the author that organic decomposition of an alkaline solution of seaweed by the action of anærobic bacteria might take place in media other than the alkaline clays suggested by Taylor. It appeared to him that the process was essentially one of hydrolysis, in which the bacteria firstly hydrolysed the fucosan or organic matter of somewhat similar chemical constitution, forming sugars—and that by further action the sugars broke down and gave rise to methane as recorded. It was found that an aqueous extract of algæ (*laminaria*) possessed an alkaline reaction. Upon exposure to the atmosphere a growth (*cladothrix dichotoma*) formed which acted upon the calcium salts of the ethereal sulphonic acids present, decomposing them with the precipitation of calcium sulphate in the form of anhydrite. At the same time the nitrogen compounds were decomposed with the formation of tertiary amines and ammonium salts. After three or four days the aqueous seaweed extract became strongly acid, due to the formation of free sulphuric acid. It was also observed that by blowing the aqueous extract with air for some time that a similar kind of reaction took place.

Assuming that in nature hydrolysis takes place over a long period of time, the aqueous extract of seaweed was submitted to prolonged acid hydrolysis. (Acid hydrolysis was chosen because of the formation of free sulphuric acid by the *cladothrix dichotoma* and also by oxidation.) Both oil and a bituminous product were formed during acid hydrolysis of the aqueous extract of algæ, but not during alkaline hydrolysis. During the acid hydrolysis, the calcium salts of the sulphonic esters were decomposed with the precipitation of calcium sulphate, and the formation of tertiary amines, and oils similar in character to naturally occurring petroleum oils. These oils and the bituminous products formed the bulk of the decomposition products of the acid hydrolysis of the algæ. It was also found that sugars themselves were decomposed during acid hydrolysis, yielding both oil and protobitumen.

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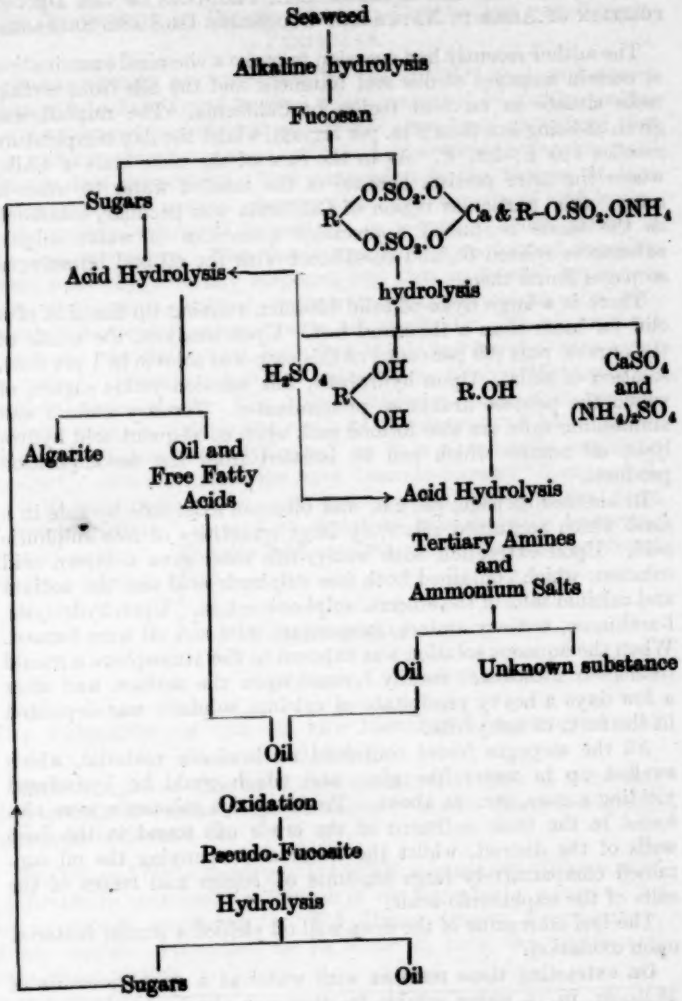
[24] *J. Coll. Agric. Imp. Univ. Tokyo*, 1816, **5**, 341–353.

THE HYDROLYSIS OF SEAWEED.



Section II.

The Presence of the Intermediate Products of the Decomposition of Algæ in Naturally Occurring Oils and Seepages.

The author recently had occasion to make a chemical examination of certain seepages of oils and bitumens and the oils from certain wells situate in an arid region of California. The rainfall was given as being less than 2 in. per annum, whilst the day temperature reaches 110° F.–120° F. As in the case of the nitre beds of Chile, where the nitre persists because of the lack of water to wash it away, this particular region of California was peculiar, inasmuch as the sands contained appreciable quantities of water soluble substances related to, and co-existent with the oil and bituminous seepages found there.

There is a large dyke of solid bitumen running up the side of a cliff for more than a thousand feet. Upon analysis, the whole of the organic part (90 per cent.) of this seep was soluble in 1 per cent. solution of soda. Upon hydrolysis, this solution yields sugars, of which the pentose arabinose predominates. Tertiary amines and ammonium salts are also formed and, upon subsequent acid hydrolysis, oil results which can be isolated from the decomposition products.

In another seepage, oil, gas, and bitumen exist side by side in a sand which contained relatively large quantities of free sulphuric acid. Upon extraction with water, this sand gave a brown acid solution, which contained both free sulphuric acid and the sodium and calcium salts of the ethereal sulphonic esters. Upon hydrolysis, l-arabinose, tertiary amines, ammonium salts and oil were formed. When the aqueous solution was exposed to the atmosphere a mould (*cladothrix dichotoma*) readily formed upon the surface, and after a few days a heavy precipitate of calcium sulphate was deposited in the form of anhydrite.

All the seepages found contained an insoluble material, which swelled up in water like glue, and which could be hydrolysed yielding sugars, etc., as above. Traces of this substance were also found in the basic sediment of the crude oils found in the deep wells of the district, whilst the water accompanying the oil contained comparatively large amounts of sugars and traces of the salts of the naphthenic acids.

The fuel oil residue of the deep well oil yielded a similar material upon oxidation.

On extracting these residues with water at a steam pressure of 25 lb./sq. in., a water soluble fraction was obtained, which upon acid hydrolysis yielded sugars, etc., as above.

Section III.

The Conversion of Oil into Bodies Resembling the Fucose-Pentosans.

It has already been recorded by the author[24] that asphaltenes change into kerols and keroles when subjected to gentle heating for a prolonged period of time. It has since been discovered that oils undergo a similar change and that oxidation plays the dominant rôle in this conversion. This conversion is the reverse of that which obtains in nature, whereby algæ, by a process of acid hydrolysis, undergo a form of degradation or reduction which results in the loss of oxygen. The kerols and keroles so formed resemble some naturally occurring seepages, and that upon acid hydrolysis they yield sugars, furfurol, tertiary amines, ammonium salts, etc., besides possessing other points of similarity. These artificial kerotenes (the class name, including kerols and keroles) also occur in nature. Twenty years ago oil gushers flooded the sands in various parts of the Elk Hills, California, and this pseudo-fucosite now abounds in the sands of the district. I have named this type of bitumen "Elkerite," as it is a naturally occurring product. As a class name the term "pseudo-fucosan" is suggested, as it yields pentose sugars upon hydrolysis, while the general term "pseudo-fucosite" is used to designate this naturally occurring type of product. Elkerite is therefore a pseudo-fucosite, produced by the oxidation of oil.

Experimental.

Section I.

The Formation of Oil by the Natural Decomposition of Algæ.

Three samples of algæ have been examined in order to show that they contain a similar range of elements to the oils and seepages examined in Section II.

The Mineral Constituents of Algæ.—The mineral constituents were qualitatively examined* in the ash of the material by means of the arc spectrum, employing an E.3 Hilger Quartz Spectrograph, which enables exploration to be made of both the visible and ultra-violet regions.

* The author is indebted to Dr. S. Judd Lewis for the spectrographical examination of the various ashes, specimens, etc.

The method has been to obtain a spectrogram of the spectroscopically standardised copper electrodes employed in juxtaposition with a composite spectrogram of the sample under investigation and of the electrodes, so that the extra lines appearing in the second spectrogram reveal the composition of the sample of material. It then remains to indentify all these extra lines, or to search for those indicative of specified elements. The latter course has been followed to the extent of searching for the thirty-four elements which were most likely to be present.

Copper is not included in the list in consequence of the equipment being furnished with copper electrodes; nor mercury, because it is not detectable by ordinary routine analysis; nor the non-metals, except silicon, boron, and arsenic.

The quantitative indications are expressed in the following terms, and deduced from the relative intensities of the spectrum lines:—

(1) Minute trace; barely definite; only just observable spectroscopally.

(2) Very slight trace; first definite indication.

(3) Slight trace, but well defined indication, probably 0·003 per cent. of the ash.

(4) Trace; well marked, though small quantity; probably 0·01 per cent. of the ash.

(5) Heavy trace; say 8 times 4; probably 0·05 to 0·15 per cent. of the ash.

(6) Very heavy trace; probably 0·2 to 0·4 per cent. of the ash.

(a little) A small proportion, such as can usually be determined by ordinary chemical processes, probably 0·5 to 2 per cent. of the ash.

Although these approximations are a very fair indication of the quantities present *in the portion* of the material *utilised* in the spectrographic experiment, they must be considered in two aspects when the results are applied to the original material: (*a*) the quantity of ash available is sometimes very small and sometimes abundant; (*b*) the proportion of ash obtained from the original material varied from a minimal proportion from an oil to the maximum in a mineral substance.

In the few cases marked "(?)" the indication is probably correct, but not sufficiently definite to leave it unqualified.

The qualification "probably" in the case of potassium, molybdenum, etc., is due to the lines of these elements, when present

in only very small proportions, being confused by closely neighbouring lines. The experimental results are detailed in the following tables :—

Elements.	1 Coorongite.	2 Macrocystis pyrifera.	3 Sargassum.
Aluminium	much	+	4+
Antimony	prob. absent	0	0 (prob.)
Arsenic	2+	+	0
Barium	4+	3+	5+
Beryllium	0	0	0
Bismuth	0	0	0
Boron	5+	5+	+
Cadmium	0	0	0
Caesium	0	0	0
Calcium	much	much	much
Chromium	2+	+	0
Cobalt	0	0	0
Germanium	0	0	0
Indium	0	0	0
Iron	much	5+	6+
Lanthanum	0	0	0
Lead	2+	+	3+
Lithium	5+	5+	3+
Magnesium	much	much	much
Molybdenum	prob. absent	0	0
Nickel	2+	0	+ (?)
Niobium	0	0	0
Potassium	prob. absent	much	0
Rubidium	0 (?)	0	0
Silicon	5+	+	+
Silver	0	+	0
Sodium	a little	much	much
Strontium	5+	much	much
Thallium	0	0	0
Tin	+	0	0
Titanium	4+	0	0
Vanadium	3+	0	0
Zinc	4+	0	6+

1. Coorongite from Australia. Dyer, *Journal of Botany*, 1872, p. 103.
2. Macrocystis pyrifera. Sample from California. Obtained from Natural History Museum, S.K.
3. Sargassum. Sample from Lake Titicaca, Peru.

Preparation of the aqueous extract of Algæ.—The sample of seaweed was collected at Brighton and the *laminaria digitata* separated and identified. After washing in fresh water to remove sand, dirt, etc., the material was spread out to dry in the air for one day. One kilo. was then placed in a linen bag and put on the perforated shelf of the autoclave in which was 1 litre of distilled water. The autoclave was then placed over a burner and heated until a pressure of 25 lb./sq. in. was registered, and then maintained at that pressure. It was observed that the liquors were alkaline to litmus after heating for two hours. The water was then changed and collected and another litre of water added to take its place

in the autoclave. After 24 hours heating at the same pressure, the liquors were neutral in reaction. The two liquors so obtained were added together, and third litre of water added. This was heated for a further 24 hours, after which the liquors were acid to litmus. The autoclave was then heated for another 24 hours, after which the liquors showed a strongly acid reaction.

Solutions made by digesting the weed for two hours only were also used in the experiments described below.

Some Properties of a Two Hour Alkaline Aqueous Extract. The Development of Acidity.

1. *On standing.*—A solution containing 1·2317 gms., of solid matter per 100 ml. was used in the following experiments :—

(*a*) No evolution of ammonia was observed on heating the solution with strong caustic soda, from which it is inferred that ammonium salts as such were absent.

(*b*) The carbylamine reaction gave a negative result, from which it is inferred that primary amines were absent.

(*c*) Tungstic acid[27] in hydrochloric acid solution gave no precipitate, from which it is inferred that tertiary amines were absent.

(*d*) After standing for one week the solution threw down a brown precipitate consisting of an organic body similar to that thrown down during acid hydrolysis, or upon the addition of sulphuric acid. Some calcium sulphate was also precipitated.

(*e*) After standing for one week, the solution gave a precipitate with barium chloride, having developed acidity during that period.

(*f*) Sulphuric and hydrochloric acids both threw down the same brown precipitate as in (*d*).

2. *On oxidation by blowing air through the aqueous solution.*

(*g*) After blowing air through the solution on the water bath for four hours the reaction became acid to litmus. After blowing for three days a precipitate was thrown down similar to (*d*).

(*h*) Free sulphuric acid developed as in (*e*).

3. *By bacterial action.*

(*i*) Upon exposure to the air in an open dish, a mould formed on the surface (*cladothrix dichotoma*). After one week the solution became acid as in (*e*), and after one month there was a copious precipitate as in (*d*).

[27] The tungstic acid used in these experiments is a colloidal solution in hydrochloric acid. It has the property of giving a bulky flocculent precipitate with tertiary amines. The reverse reaction is used in the separation of tungsten from other metals in its ore ; in this case the tungsten is precipitated by the addition of quinoline.

The Acid Hydrolysis of Algæ.—Because of the tendency of aqueous extracts of algæ to change their character from the alkaline to the acid condition as described, it was considered that alkaline hydrolysis in nature must of necessity be of short duration. The available time for subsequent acid hydrolysis is unlimited. Because of the formation of free sulphuric acid it was considered that this acid was the actual hydrolysing agent which brought about the changes in the chemical constitution of the algæ in nature.

The Acid Hydrolysis of the two-hour Alkaline Aqueous Extract of Seaweed.—The addition of 5 per cent. by weight of sulphuric acid to one litre of the alkaline extract caused the precipitation of 0·396 gms. of a brown precipitate of algarite. (See definition and p. 77.) Hydrochloric acid precipitated the same material in approximately the same quantity (0·389 gms.). This precipitate was filtered off. The filtrate was treated with various reagents, whose reactions are given below, and also one litre was hydrolysed for two days, and another litre for seven days by gentle boiling under a reflux condenser. A skin formation was noted on the sides of the flask as observed by Haas and Wells.[16]

At the end of these periods of time the freshly formed algarite was filtered off and the filtrates were treated with reagents, and the following table shows the difference in their behaviour as hydrolysis proceeds. The oil formed during hydrolysis appears in the table as "Chloroform Extract," and for convenience, all results are calculated on the litre basis.

The Acid Hydrolysis of Seaweed Residues.—In order to ascertain whether oil could be obtained from the dried seaweed residues remaining after their exhaustive extraction as on p. 89 in the autoclave as described, 100 gms. of the dried weed were hydrolysed for a period of four days with one litre of a 5 per cent. by weight solution of sulphuric acid, then filtered through a Buchner funnel. 44·3 gms. of residue remained, and the balance of 56·7 gms. was dissolved in the acid filtrate. Both the residue and filtrate were extracted with chloroform, which dissolved out the oil formed during hydrolysis. The following results were obtained :—

Solvent.	Residue.	Acid Filtrate.
Chloroform.	3·6 gms oil.	0·84 gms oil.

THE NATURE OF THE PRODUCTS OF ACID HYDROLYSIS OF ALGÆ.

1. *The Brown Bituminous Substance—Algarite.*—It is proposed for convenience to call this brown precipitate "Algarite" for reasons which will be explained later.

The Acid Hydrolysis of the 2-hour Alkaline Aqueous Extract (12·31 gms. Solids/Litre) of Seaweed.

Reagent used.	Before acid hydrolysis.			After two days' hydrolysis.			After seven days' hydrolysis.		
	Weight in gms. of precipitates, organic matter and ash, calculated per litre of solution.								
	Precipitate.	Organic matter.	Ash.	Precipitate.	Organic matter.	Ash.	Precipitate.	Organic matter.	Ash.
Sulphuric Acid									
Yielding algarite	0·396	0·369	0·027	0·934	0·819	0·115	5·354	5·297	0·057
Ethyl Alcohol.									
Yielding the calcium salts of the sulphonic esters ..	3·518	2·530	0·988	2·740	0·909	1·831	1·628	0·074	1·554
Tungstic Acid.									
Yielding tertiary amines ..	nil.	nil.	nil.	2·722	1·488	1·234	2·294	1·098	1·196
Ammonia.									
Yielding ammonium salts (?)	nil.	nil.	nil.	0·242	0·203	0·039	nil.	nil.	nil.
Chloroform.									
Extracing oil and fatty acids	nil.	nil.	nil.	0·626	0·626	0·000	1·274	1·274	0·000

After seven days acid hydrolysis the two-hour alkaline extract of seaweed, a total weight of 5·35 gms. were obtained from 12·31 gms. of soluble seaweed material; equivalent to a 43·2 per cent. yield. The ash content consisted mainly of calcium sulphate, which amounts to 0·6 per cent. in algarite washed with excess of boiling hydrochloric acid. In freshly precipitated algarite the ash content is 3·9 per cent.

Algarite is a brown amorphous powder, which appears yellow under the microscope and shows no sign of structure. It is very sparingly soluble in ethyl and amyl alcohols, and is insoluble in ether, carbon disulphide and chloroform. Algarite, as formed during hydrolysis at 100° C., is partially soluble in pyridine (24·8 per cent.) (c.f. algarose, p. 96) and this soluble portion has all the characteristics of a bitumen, particularly that class known as the keroles. The insoluble portion also resembles some classes of bitumen, and in particular a bitumen called McKittrite, which is described later. Algarite is readily soluble in a dilute soda solution, from which it is almost entirely reprecipitated by acids, as a dark red powder, possessing acidic properties. It appears to be the acid of a body related to the fucose-pentosans, for on hydrolysis with soda it reduces Fehling's solution and yields osazones with phenyl hydrazine acetate. It is not yet proven that the substance is a pentosan, but at this stage it is only assumed to be a pentosan by analogy with a seepage bitumen having similar properties which yields the pentose arabinose upon hydrolysis. (See sample No. 6.) Upon dry distillation oil is evolved in quantities (45 per cent. yield) while traces of both hydrogen sulphide and ammonia are evolved. The oil so evolved contains appreciable amounts of tertiary amines as shown by the tungstic acid test, while phenols were present in the alkaline wash. The odour evolved during dry distillation is that of burnt feathers. Algarite is also slightly soluble in hot water and dilute acids, and after prolonged acid hydrolysis traces of oil can be extracted from the liquors by chloroform.*

Being partially soluble in pyridine but insoluble in chloform or carbon disulphide, algarite must be classified as a kerole and, on account of the low sulphur content, the classification can be carried one step further—it is an oxykerole.

The Ethyl Alcohol Precipitate.—This material is described by Haas and proved to consist of the calcium salts of the ethereal sulphonic esters. The ash consists mainly of calcium sulphate. When dry, the material is a light brown amorphous powder, soluble

* Haas and Wells [14] noted the formation of the brown amorphous powder during the acid hydrolysis of seaweed in 1923, but the yield was small owing to the short time of hydrolysis, and the substance was not examined.

in both dilute acids and alkalis as well as in water. Upon hydrolysis, it yields sulphuric acid, calcium sulphate, and a dihydric alcohol, which upon further hydrolysis forms tertiary amines as proved by the tungstic acid reaction, and ultimately yields oil and sugars. The progress of the decomposition is shown in the table "Acid Hydrolysis," p. 92.

The Tungstic Acid Precipitate.—This material consists of a black amorphous powder soluble in acetone. The nitrogen present is in the form of tertiary amines, and also, probably, as the ammonium salt of a sulphonic ester, because upon boiling with alkali ammonia is evolved.

Upon boiling with strong caustic soda (33 per cent.) a dark coloured oil is liberated.

If the tungstic acid precipitate be dissolved in ammonia and reprecipitated by the addition of hydrochloric acid, tungstic acid is thrown down, and after filtration a brown solution remains which, upon evaporation, gives an oily residue, soluble in ethyl and amyl alcohols, but insoluble in chloroform, benzene, and carbon disulphide.

The Ammonia Precipitate.—This precipitate was obtained by neutralising the acid solution with ammonia. It is a black amorphous powder, which decomposed on drying in the water oven yielding an oil soluble in chloroform. It is only partially soluble in ether and petroleum ether, the insoluble residue having the properties of asphaltenes.

The Oil.—The oil was obtained from the acid solution by extraction with chloroform, and amounted to practically 10 per cent. by weight of the total solids originally present in the solution. This however, is not a true measure of the amount of oil that could have been obtained had hydrolysis proceeded still further. Nor does this amount of oil represent all that can be obtained from the aqueous extract, for, as recorded, both the tertiary amines and the ammonia precipitate can be made to yield their quota of oil. Under the microscope the acid solution appeared to contain the oil in an emulsified form. The oil was a deep, lemon yellow viscous liquid, having the appearance of a heavy spindle oil. It was fairly stable towards strong sulphuric acid. It was partially soluble in caustic soda solution showing the presence of the naphthenic acids, and was totally soluble in ethyl ether, petroleum ether, carbon disulphide, and chloroform.

The percentage of naphthenic acids represented 21·8 per cent. of the total oil, and were of a reddish-brown colour and liquid at normal temperatures. The remaining hydrocarbon oils (78·2 per cent.) were stable to sulphuric acid.

The Sugars.—As a relatively large amount of sugars remained in the acid solution after hydrolysis, experiments were made to ascertain if the sugars themselves played any important part in the formation of either oil or bitumen, even though this seemed unlikely. At the same time, the hydrolysis of sucrose by acid, with the formation of glucose and fructose is well known, as is also the production of water soluble ketonic acids such as pyruvic and laevulinic acids.

In the first experiment 100 gms. of sucrose were placed in a flask with 250 ml. water and 10 ml. of sulphuric acid and boiled under a reflux condenser. After half an hour the solution darkened and a skin of a semi-plastic asphaltic looking material formed on the surface of the liquid. After hydrolysing for 24 hrs. this substance became harder, and by appearance it resembled the char obtained by the action of strong sulphuric acid on sucrose; 15 gms. were obtained after filtering off, washing with water until neutral, and subsequently drying.

The precipitate was not, however, a purely carbonaceous mass, as it was partially soluble in pyridine; 5·01 gms. giving 1·17 gms. of soluble material, equal to a 23·4 per cent. yield. This pyridine soluble fraction dissolved in chloroform, alcohol, ammonia, and caustic soda solution, and was partially soluble in ether. It contained no sulphur. After being dissolved in caustic soda the substance rapidly reduced Fehling solution.

The filtered acid liquors were a dark brown colour, and after repeated extractions with chloroform a water-insoluble red oil was isolated, amounting in all to 5·9 gms.

After the isolation of the oil a portion of the remaining acid liquor was placed on the water bath and allowed to concentrate. As the acid grew stronger the mass became blacker and blacker, resulting in a quantity of a rubber-like material gelatinous to the touch as it also was in appearance, and resembled fucosite after it had swelled in water.

An excess of lime was added to another portion in order to neutralise the free acid and to form the calcium soaps of the gelatinous-like material mentioned above. Lime was chosen both on account of the natural occurrence of calcium salts in contiguity with the oil and seepages described later, and also on account of the fact that algæ contain such a large amount of lime in their inorganic constitution.

After drying on the water bath, the above residue was placed in a flask and heated at 110° C. for one week. Water, but no oil was evolved. When this thoroughly dried residue was heated in an ignition tube a reddish-brown oil was given off with every appearance of the oils from the seepages described in section 2 of this paper. The odour was that of burnt feathers which was remarkable because

no nitrogen was present. Neither the cane sugar, the sulphuric acid nor the lime contained nitrogen. This explains the reason of the burnt feather odour of the oils evolved on heating these seepages, which contained only normal amounts of nitrogen; *e.g.*, the fucosite described later (p. 105) only contained 1.72 per cent. N., but on heating evolved a strong characteristic odour of burnt feathers.

On account of this similarity, another experiment was undertaken to ascertain if this precipitate could not be obtained in an uncharred condition, and also to see if it resembled algarite because of the similarity in behaviour to pyridine and other solvents.

One hundred gms. sugar, 300 ml. water, 100 ml. sulphuric acid, and 400 ml. chloroform were placed in a flask under a reflux condenser and heated so that the chloroform was just kept boiling, whereby the temperature of the contents of the flask was maintained at the boiling point of the chloroform, *viz.*, 61° C. At the same time, the products of reaction were removed by the condensed chloroform vapour from the sphere of chemical action and so preserved from the further action of the acid. Under these circumstances the precipitate appeared as a flocculent red-brown feathery substance, and simultaneously the chloroform became firstly a light red, and finally a dark red-brown colour, as it dissolved the oils formed. After the first day the whole was filtered through a large Buchner funnel and the precipitate dried and weighed. The chloroform extract was separated from the acid liquors in a separating funnel, washed with a little water, distilled in a weighed flask, thus giving the weight of the oil formed. This precedure was repeated daily and the following results obtained:—

	1st day.	2nd day.	3rd day.	4th day.	5th day.	6th day.	7th day.	8th day.	Total.
Wt. of algarose	0·27	2·34	2·11	0·44	1·56	0·23	0·27	0·1	7·52
Wt. of oil in gms.	1·006	4·5	2·87	1·5	4·21	2·26	1·21	approx. 0·57	18·126

The Properties of Algarose.—This precipitate, to which it is proposed to give the generic name "Algarose" may be taken to be a pure form of Algarite, both as obtained from seaweed and from naturally occurring seepages, such as exemplified in McKittrite (Sample No. 6). The termination "-ose" indicates its relationship to the sugars. It differs in some respects from algarite inasmuch as it may be considered a chemically pure bitumen, if not a synthetic one, as it has been prepared from a substance of known constitution. It contains neither rare elements, tertiary amines, ammonium salts, calcium salts of the ethereal sulphonic esters, nor sulphur.

As freshly precipitated from low temperature solution algarose is a red-brown powder wholly soluble in pyridine, ammonia, caustic soda, and alcohol, but after drying or heating in the water oven for

a few hours it firstly becomes only partially soluble, and finally insoluble in these solvents. The solution in caustic soda readily reduces Fehling solution, as also does the aqueous or slightly acid solutions in which algarose is sparingly soluble. If, after drying, it be attempted to dissolve algarose in an aqueous or soda solution, it swells up to a rubber-like mass increasing its volume two or three times as does the fucosite of Samples Nos. 1, 2 and 3.

Upon dry distillation vapours are given off which condense as a red oil. The smell resembles that of burnt sugar in the first place but later the biting smell of pyruvic acid disappears and the odour more nearly resembles that of some asphaltic residues. A residue of carbon remains.

As algarose is soluble in alkalis, from which solutions it is reprecipitated by acids, its nature is acidic. It has not yet been ascertained whether this acidity is due to the presence of a carboxylic group, or whether it is due to the ketonic formation

$$—CO.CH_2.CO—$$

neither has it been ascertained whether its power of reducing Fehling solution is due to the presence of an aldehyde or of the ketonic grouping

$$—CO.CH_2.OH$$

as occurs in fructose.

Upon oxidation with nitric acid, a crop of crystals was obtained which were colourless prisms melting at 100° C., and which, when dissolved in water, precipitated an ammoniacal solution of calcium chloride. They were therefore oxalic acid.

The Properties of the Oil derived by the Acid Hydrolysis of Sugar (Sucrose).—The oil is a dark red liquid, very similar in appearance to the oil and asphaltene fraction of McKittrite. It is acidic in character, dissolving in caustic soda solution and also in ammonia, with considerable darkening in colour. On acidification a brown-red precipitate is thrown down similar in appearance to algarose. Whether this change in physical properties is due to tautomerism or to polymerisation is at present unknown.

On heating in the water oven algarose becomes insoluble insolvents and here the change may also be similarly due to tautomerism. The oil is not a pure chemical substance, but a mixture containing :—

Unsaponifiable matter (A light coloured oil of waxy appearance).	1·20	per cent.
Asphaltenes (Soluble in CS_2)	1·12	„
Kerotenes (Soluble in $CHCl_3$).	14·28	„
Oil (Soluble in ethyl ether .	83·40	„

The oil is soluble in alcohol, chloroform and pyridine, and is sparingly soluble in carbon disulphide, water, and dilute acids; it is insoluble in petroleum ether. It is readily soluble on alkalis, and this solution reduces Fehling solution. (These characteristics are similar to those of the asphaltene fraction of McKittrite.)

If, however, the oil be first dissolved in ammonia and evaporated to dryness on the water bath, the resultant mass is a dark brownish black coloured solid, fairly soluble in water; this aqueous solution does not reduce Fehling. In this respect the formation of ammonium salts during the hydrolysis of seaweed is of importance; 14 gms. of oil were distilled at atmospheric pressure, with the following results:—

Initial boiling point.		82° C.
— 100° C.	0·5 ml. = 3·5	per cent.
100 — 200° C.	1·1 ml. = 7·2	,,
200 — 220° C.	6·3 ml. = 45	,,

At 220° C. the residue suddenly changed into a solid form (44·3 per cent.), insoluble in soda and pyridine.

The 6·3 ml. fraction was 40 per cent. soluble in soda, and like the original oil the addition of acid caused a brown solid precipitate to be thrown down. The remaining 60 per cent. of this oil was soluble on strong sulphuric acid.

As the oil was totally soluble in soda before distillation, it is evident that an intramolecular change has taken place. The acidity may have been destroyed either by the elimination of the carboxylic group —COOH or by the tautomeric change

$$R - C(OH) = CH - CO \rightleftarrows R - CO - CH_2 - CO -$$

These hydroxy acids are not difficult to reduce. The classic example is the reduction of all the >CH.OH and $-CH_2OH$ groups by means of hydriodic acid and amorphous phosphorus.

$$CH_2OH\cdot(CH\cdot OH)_4\,CH\cdot OH\,COOH + 12HI = CH_3\,(CH_2)_4\cdot CH_2\cdot COOH + 6H_2O + 6I_2$$

n. heptylic acid

When the acids were placed in the air-oven at 110° C. for one week, 49 per cent. by weight were converted into a solid material insoluble in both caustic soda and chloroform. In appearance it resembled the insoluble variety of algarose resultant upon the gentle heating of the same at 110° C. for a prolonged period of time. The remaining 51 per cent. consisted of an oily looking substance of an acidic nature as it was totally soluble in soda.

When the acids were heated with calcium chloride under the same conditions, approximately the same amount was changed

into the insoluble variety of algarose, but a large part (42 per cent.) of the remainder was an oil insoluble in soda, but soluble in chloroform. The acids had thus been converted into an inert neutral hydrocarbon oil by the agency of a material—calcium chloride—which is found associated with oil in nature.

The oils firstly obtained from the sugars are soluble in soda and have the properties of carboxylic acids, but readily decompose, yielding oils insoluble in soda and stable to sulphuric acid; the oils then possess the properties of hydrocarbon oils. In the same way the oil obtained from the acid hydrolysis of the algæ contained 21·8 per cent. of acids, which are indiscriminately called carboxylic or naphthenic acids by custom. During decomposition it is to be expected that the carboxylic group would decompose with the evolution of carbon dioxide. In this respect it is interesting to note that the gases obtained from the oil wells of the district are characterised by their large carbon-dioxide content. (See p. 100.)

The Alkaline Hydrolysis of the Aqueous Extract of Seaweed.—During the alkaline hydrolysis of seaweed, algarite is not precipitated on account of its solubility in soda. Whether it is actually formed or not is unknown. At the time these experiments were in progress the formation of algarose from sugar had not been discovered, and the importance of looking for the substance had not been recognised.

As in the case of acid hydrolysis it is found that the calcium salts of the ethereal sulphonic esters were decomposed, tertiary amines being simultaneously formed. Ammonia is also liberated in small quantities, but no neutral oils were formed soluble in chloroform. The sodium salts of the fatty acids did not appear to be present, as nothing was extracted by chloroform after acidification.

The two hour alkaline aqueous extract employed during these experiments was part of the same stock as that employed for the experiments upon acid hydrolysis. The following results were obtained :—

The Alkaline Hydrolysis of the Aqueous Extract of Seaweed.

Reagent.	Aqueous extract; 1·213 gm. solids per 100 ml.			Aq. extract plus 2 per cent. sodium carbonate after four days' hydrolysis.		
	Weight of precipitate.	Organic matter.	Ash.	Weight of precipitate.	Organic matter.	Ash.
Ethyl alcohol..	0·3518	0·2530	0·0988	0·1352	0·1240	0·0112
Tungstic acid..	nil.	—	—	0·4584	0·2092	0·2492
Ammonia ..	nil.	—	—	nil.	nil.	nil.
Chloroform ..	nil.	—	—	nil.	nil.	nil.

Analyses of Natural Gas from the Western Part of the Sunset-Midway Field.

	Percentage CO_2.
1. Chanslor-Canfield Midway Oil Co., well 6, sec. 31, T31S., R.23E. Gas associated with oil of 22° B. gravity, chiefly in zone C. Sampled by G. S. Rogers, July, 1914; analysed by G. A. Burrell, Bureau of Mines	19·7
2. Hawaiian Oil Co., well 1, sec. 31, T31S., R.23E. Sampled by I. C. Allen, July, 1909; analysed by G. A. Burrell, Bureau of Mines	10·5
3. Hale-McLeod Oil Co., well 5, sec. 8, T32S., R.23E. Gas associated with oil of 17° B. gravity in zone A. Sampled by G. S. Rogers, July, 1914; analysed by G. A. Burrell, Bureau of Mines	20·0
4. Indian and Colonial Oil Co., well 23, sec. 22, T32S., R.23E. Gas associated with oil of 14° B. gravity in zone A. Sampled by G. S. Rogers, July, 1914; analysed by G. A. Burrell, Bureau of Mines	9·8
5. Kern Trading and Oil Co., wells in sec. 31, T12N., R.23W. Gas associated with oil of average gravity of 21° B. in zone B. Sampled and analysed by W. E. Perdew; authority, Kern Trading and Oil Co.	22·8
6. Topaz Oil Co., well 3, sec. 18, T11N., R.23W. Gas associated with "shale oil" of 17° B. gravity in zone B. Sampled by G. S. Rogers, July, 1914; analysed by G. A. Burrell, Bureau of Mines	24·2
7. Sprecels Oil Co., well 5, sec. 32, T12N., R.23W. Gas from bed 80 ft. above producing oil sand (in zone B). Sampled by G. S. Rogers, July, 1914; analysed by G. A. Burrell, Bureau of Mines	20·0

Analyses of Gas from the Southern Part of the Buena Vista Hills, Midway Field (T32S., R.24E.).

	Percentage CO_2.
1. Honolulu Oil Co., well 7, sec. 4. Gas about 300 ft. above top of oil zone B	4·2
2. Honolulu Oil Co., well 1, sec. 6. Dry gas about 200 ft. above top of oil zone B. *California State Min. Bur. Bull.*, 1914, **69**, 250	7·0
3. Honolulu Oil Co., well 5, sec. 6. "Dry" gas about 200 ft. above top of oil zone B. Sampled by G. S. Rogers, July, 1914; analysed by G. A. Burrell, Bureau of Mines	7·6
4. Honolulu Oil Co., well 7, sec. 6. "Wet" gas associated with oil of 31° B. gravity, chiefly in zone C	16·5
5. Honolulu Oil Co., well 5, sec. 8. Gas about 250 ft. above top of oil zone B	8·1
6. Honolulu Oil Co., well 6, sec. 8. Gas about 400 ft. above top of oil zone B	6·9
7. Honolulu Oil Co., well 7, sec. 8. Gas about 300 ft. above top of oil zone B	5·6
8. Honolulu Oil Co., well 1, sec. 14. Gas about 1000 ft. above top of oil zone B	7·7

Experimental.

Section II.

The Presence of Algæic Decomposition Products in Natural Oils and Seepages.

The following is a list of the samples examined. All were obtained from the Elk Hills, California, and labelled as indicated :—

1. A sample (sec. 32, T30S., R.24E.) of clay, some of which is clean, some of which is stained dark brown, and on some of which is a laminated black substance in the fissures of the clay itself. The clean clay is of a battleship grey colour, slightly tinged with blue.
2. A sand (sec. 32, T30S., R.24E.) which is stained throughout by a brown or black coloration, containing laminæ of a spongy black material which can partially be separated from the sand by washing.
3. A clay (sec. 32, T30S., R.24E.), "Old Pit Clay," relatively more discoloured by the black material than sample No. 1.
4. A sample (sec. 14, T30, R.22), pebbles derived from a fault at the S.W. corner.
5. A sand (sec. 11, T32S., R.24E.), "Buena Vista Blowout," impregnated with oil and containing free acid. It is brown and contains numerous white specks.
6. A solid bitumen or a heavily organic bituminous shale (Sect. 28, T30, R22), "McKittrick Dyke." This bitumen is of a decided brown colour similar to freshly precipitated ferric hydroxide. It is brittle and fissured; along the lines of fissure there is a light grey colouration. The inorganic matter is a diatomaceous earth.
7. A Black Sand from Lamont Cut (sec. 32, T30S., R.24E.).
8. A Clean Sand from Lamont Cut (sec. 32, T30S., R.24E.).
9. Clean Sand Cut No. 1. This cut being on the same side of the gulch and north of Lamont Cut.
10. Clean Sand Cut No. 2 on the opposite side of the gulch from the Lamont Cut and below cut No. 3.
11. Clean Sand Cut No. 3. On the same side of the gulch and higher up the hill than Cut No. 2.
12. 3 samples of oil and sludge from the tanks of Well No. 7, situated in the S.E. ¼ of the S.E. ¼ of the N.W. ¼ Sect. 1, T31S., R.24E.

13. 2 samples of oil and sludge from the tanks of Carmen Oil Well No. 5. sec. 36, T30S., R.24E.

14. 2 samples gas, one from Well No. 7 (sample 12) and one from Well No. 74, sect. 31, T30S., R.24E.

The Presence of the Calcium Salts of the Ethereal Sulphonic Esters.—The presence of this type of salt is illustrated by samples Nos. 5 and 13.

Seepage No. 5 is a dark brown sand containing a number of white specks, which proved on examination to be calcium sulphate. Quantities of gas were evolved from the sand which contained 12 per cent. of oil, of a character similar to that obtained from wells samples Nos. 12 and 13. The sand also contained relatively large quantities of free sulphuric acid, which destroyed the paper and linen containers in which the samples were packed. On washing the sand with water, a brown solution containing 1·82 per cent. of organic matter was obtained, calculated on the sample, which upon evaporation formed a jelly. The sand also contained small quantities of a substance which swelled up in water, and also a bituminous material of the nature of an oxykerite, and which is described later.

The Aqueous Extract.—A quantity of aqueous extract was made by enclosing the sand in a linen bag and placing the same in an autoclave containing water. The water was boiled until the steam pressure registered 25 lb./sq. in., and after being maintained at that pressure for one hour the autoclave was allowed to cool, and the water collected. This acid aqueous extract was concentrated, and, on the addition of excess of alcohol, a light brown flocculent precipitate was thrown down. This precipitate was filtered off, redissolved in water, and reprecipitated twice by alcohol. The precipitate was then white in colour, and the aqueous solution gave a neutral reacton.

Upon hydrolysis in a 5 per cent. by weight sulphuric acid solution, it was noticed that a skin formed on the surface of the liquid in the same way as it forms on the surface of the aqueous seaweed extract. Hydrolysis was continued for four days, during which time a precipitate resembling algarite was thrown down, separated and filtered off. The filtrate contained sugars, reduced Fehling solution, and yielded an osazone of a mixed nature; it gave a precipitate with tungstic acid, thereby indicating the formation of tertiary amines, and also yielded a precipitate when neutralised with ammonia. The ammonia precipitate yielded appreciable quantities of oil on drying in the water oven.

A light-coloured oil was extracted from the hydrolysed liquors by means of chloroform in comparatively large quantity. As all these reactions point to the substance being the calcium salt of the ethereal sulphonic esters, the ash content (11 per cent.) was examined and found to consist wholly of calcium sulphate.

Sample No. 13.—When the fuel oil residue (boiling over 300° C.) of this sample of oil was heated with water in an autoclave to 25 lb. steam pressure for 24 hours, partial solution of the oil took place. The aqueous solution was alkaline, and when neutralised threw down a thick, flocculent, buff-coloured precipitate soluble in boiling water, and reprecipitated by alcohol. 1000 ml. of fuel oil were extracted and 11 gm. of this water-soluble material was obtained. This precipitate contained 22·8 per cent. of ash which contained calcium, iron magnesium, etc. The calcium present was in the form of the sulphate. The precipitate was washed with chloroform to remove traces of adherent oil, and was then hydrolysed with a 5 per cent. sulphuric acid solution as before. The resultant solution contained tertiary amines, sugars and yielded oil upon chloroform extraction as in the case of sample No. 5.

The Presence of Free Sulphuric Acid.—The presence of free sulphuric acid is best exemplified in the case of sample No. 5. An aqueous extract of this sand is strongly acid to litmus, and gives a heavy precipitate with barium chloride in the presence of nitric acid.

The Presence of Calcium Sulphate.—Calcium sulphate is distributed throughout sample No. 5 as white specks. Strong hydrochloric acid dissolved the major part out, and both the calcium and the sulphate radicle were identified in the solution.

The Presence of Sugars.—The presence of sugars in a combined form was found in all except the gaseous samples. Sugar was found in the free state in one instance.

Sample No. 13.—The water that accompanied the oil drawn from the well separated out in the settling tank, and when tested was found to reduce Fehling's solution, and to give osozones with phenyl hydrazine acetate. This is the only instance where sugars were found directly as such. 27 ml. of water were present in the 1-gall. oil can in which the sample was dispatched, and was too little to permit quantitative determinations to be made.

Samples Nos. 1, 2, 3, 7, 8, 9, 10, 11. *Definition.*—The brown or black material found in the above sands and clays will be proved to be a partly hydrolysed fucose-pentosan, intimately mixed with its own decomposition products, of which oil, naphthenic acids, and an oxykerite may be mentioned. This oxykerite is the predominating decomposition product, and is formed, as shown later,

by the prolonged oxidation of the oil at low temperatures. The bulk of the material is, however, the partly decomposed pentosan fucose, and hence, for the sake of convenience, the black material will be called "fucosite."

The oxykerite, mentioned above, is common to all the other seepages, and as it has its own peculiar properties it is proposed to call this material "elkerite." The termination "ite" is used in both cases to indicate the relationship of these substances with naturally-occurring kerites.

The fucosite found in the sands ran vertically through the beds. It was laminated and, in some cases, could be peeled off in sheets of up to ¼ in. in thickness, to which a quantity of sand still adhered. On being placed in a beaker and covered with water, it swelled up to six or seven times its natural size, and had the appearance of a brown, gelatinous, laminated mass. It was tough like soft india-rubber. The inside of the mass was comparatively free from sand. All the fucosite was not in a laminated condition. The mode of its disposition suggested a fluid carrying a solid in suspension, which had forced its way through a series of fissures, thus giving the laminations, and to some extent, into the surrounding porous sand and deposited its solid matter in the interstices, a condition which would obtain if the sand had acted as a filter.

The so-called "clean" sands also had minute quantities of fucosite distributed throughout the beds. It had a tendency to collect in those places where the sand contained small quantities of clay, which held up and adsorbed the material and its decomposition products during their passage through it. The distribution of fucosite in the clay samples was similar to that existing in the sands. There were black veins of the material, and a brown colouration permeating the clay for distances between ¼ in. and 2 in. around the fissure.

The Separation of Fucosite.—The separation of fucosite from the accompanying sands was carried out in the following manner.

The sand was soaked in water for one week, when the fucosite swelled up and pieces varying in size, up to $1 \times 1 \times \frac{1}{4}$ in., could be picked out by hand. The whole was filtered through a 40-mesh gauze, which passed most of the sand and retained the fucosite, still mixed with some of the larger particles of sand. The mixture was placed in a glass tube 1 metre long and 4 cm. diam., at the bottom of which was a water inlet connected to the high-pressure water tap. By adjusting the velocity of the water running through the tube a very good separation could be affected.

In the case of the clays two or three grams of fucosite were collected by breaking the clay at the fracture, and levering up the laminæ with a penknife.

In the case of the "clean" sands the procedure followed was to look for stained portions, if any, and to subject them to the water elutriation described. Some of the sands, however, appeared to be entirely clean; and in this case the whole was stained by an alcoholic solution of erythrosine, and allowed to stand in a warm place for a day. The sand was then transferred to a 200-mesh gauze and washed with cold water until clean and free of dye. Numerous samples were then taken and examined under the microscope, by means of which the focusite—now stained pink—could be readily identified. The fact that fucosite is opaque to polarised light was also very helpful in its identification.

Microscopical Examination.—Prof. Tabor, of the Imperial College of Science and Technology, reports that "On microscopic examination this material proves to be wholly composed of a unicellular blue-green alga, belonging to the family of cyanophycæa, and is therefore entirely of vegetable origin." Mr. Tandy, of the British Museum (Natural History), partially supports this view after an examination of microtome sections cut at 10 μ, and reports that the material does not wholly consist of *cyanophycæa*. Dr. Wade also examined the specimens and reported that the material consisted wholly of blue-green algæ.

Interspersed throughout the mass there were pieces of elkerite.

Properties.—The physical properties of fucosite have already been described.

Fucosite contains approximately 0·5 per cent. of oil soluble in carbon disulphide.

Upon dry distillation fucosite yields an oil very much resembling that obtained from peat. The yield was approximately 25 per cent. of the dry weight of the fucosite. There was not enough of the original material to obtain enough oil upon which to carry out the usual physical determinations, but there was just enough to be dried and to give an ultimate analysis: C, 78·1 per cent.; H, 10·2 per cent.; O, 8·08 per cent.; N, 1·72 per cent.; S, 1·90 per cent.

The gas evolved during the dry distillation had the following composition, the analysis being carried out in a Bone-Wheeler gas analysis apparatus. CO_2, 55·2 per cent.; H, 14·06 per cent.; C_nH_{2n+2}, 15·0 per cent.; C_nH_{2n}, 3·2 per cent.; CO, 8·1 per cent.; N, 4·5 per cent.; H_2S, nil.

When fucosite is burnt the odour evolved is that of burnt feathers. The material is readily soluble in dilute alkalis from the solution of which it is precipitated by acids. It is very sparingly soluble in water, dilute acids and organic solvents.

In one experiment 10 gms. of fucosite obtained from sample No. 2 were placed in an Erlenmeyer flask and hydrolysed with 100 ml. of a 3 per cent. solution of hydrochloric acid for four hours, under a reflux condenser. The hydrochloric acid solution rapidly turned a lemon-yellow colour, and ultimately a port wine red. The contents of the flask were then filtered and evaporated down on the water bath. the liquors smelling strongly of burnt sugar. Some needles separated out after cooling overnight and were hand-picked next morning. These were carefully recrystallised from about 10 ml. of water and dried in the desiccator. The melting point was 157° C.; arabinose requires 159–160° C.

The remaining solution was then diluted and decolorised with animal charcoal, and filtered. The filtrate rapidly reduced Fehling solution, and yielded an osazone with phenyl hydrazine acetate. This osazone was of an orange colour, but after recrystallisation from hot water the colour was a lemon yellow. The crystals were dried overnight in the desiccator, over sulphuric acid. m.pt.= 157–158° C.; arabinose requires m.pt. 158–159° C.

Another osazone was also obtained, melting at 127–134° C. Fucosazone melts at 130–140° C.

The decolorised liquor was also tested in the polariscope, and found to be slightly lævorotatory. The quantity of material in the decolorised liquor was unknown, the volume was 10 ml., and the rotation was —1·7°.

A similar hydrolysis was made with hydrochloric acid having a specific gravity of 1·06, refluxing taking pace for a period of four hours. After filtration the liquor was distilled and the distillate gave the furfural reaction by turning an aniline acetate paper pink.

The formation of oil from fucosite was proved: 10 gms. were hydrolysed with a 5 per cent. solution of sulphuric acid for one week. From the filtered liquor 1·23 gms. of an oil similar to that described as having been obtained from seaweed was obtained by extraction with chloroform.

As before mentioned, fucosite contains traces of free oil which can be obtained by extraction by carbon disulphide in a Soxhlet apparatus. The yield varies from 0·3 to 0·5 per cent. on the dried weight of the material.

Traces of free naphthenic acids are also present in fucosite. These can be isolated by extracting the solution obtained upon acidifying a freshly-made alkaline solution of the material with chloroform. The isolated acids are dark brown in colour, soluble in soda, etc., and possess the characteristic odour.

Upon hydrolysing fucosite for two days in acid solution the formation of the calcium salts of the ethereal sulphonic esters was

shown by the formation of a precipitate thrown down by ethyl alcohol. Tertiary amines and ammonium salts were also formed as well as the sugars described above.

By alkaline hydrolysis with a 2 per cent. sodium carbonate solution the above bodies were also formed, with the exception of oil, which as previously remarked does not appear during alkaline hydrolysis. Remembering the formation of naphthenic acids during acid hydrolysis of algæ, it is, of course, possible that the sodium salts of these acids are formed.

Sample No. 6.—The solid bitumen from the McKittrick Seep is a brown, friable material, on the fissures of which is a greyish-yellow coating of elkerite. As this bitumen proves to be an oxy-kerite, it is proposed to call it " McKittrite," as it possesses several distinctive properties.

On heating, McKittrite swells, and sinters at about 200° C., giving off a faint odour of burnt feathers. Upon ignition it yields an ash—16 per cent.—consisting of sand, clay, and calcium sulphate. The percentage of ash in the kerite itself, is small—0·31 per cent.—and this contains comparatively large quantities of vanadium and the rarer elements.

The organic matter, of which this kerite is composed, is made up of :—

Fucosite (insol. in org. solvs.) (Kerenes)	13·28 per cent.
Keroles—smiliar to algarite (sol. only in pyridine)	2·72 ,,
Kerols (sol. in pyridine and chloroform)	48·6 ,,
Asphaltenes (sol. in pyridine, chloroform, carbon disulphide)	35·4 ,,

The fucosite was obtained, along with the inorganic matter, after extraction firstly with chloroform and then with pyridine. The insoluble mixture was then boiled with hydrochloric acid to remove soluble inorganic matter, and the organic matter left contained only heavy particles of sand which were separated by decantation with water. The bulk of the organic matter consisted of fucosite, and could be readily identified under the microscope by the spotted, bubbly appearance of its yellow laminæ. It contained, also, quantities of elkerite, which were identified by the plain, transparent yellow plates of irregular shape. The fucosite so obtained was readily soluble in soda solution.

The Keroles and Kerols were black amorphous powders, soluble in their respective identifying organic solvents, as also in aqueous sodium hydroxide solution. The keroles swell and sinter at 220° C., while the kerols swell and sinter at 180° C. On further heating they evolve water, oil, traces of ammonia, and sulphuretted hydrogen.

The asphaltenes are of a deep red colour, and have the appearance of a semi-solid asphaltic bitumen, with the exception that they are much more transparent to light than is usually the case. They are soluble in carbon disulphide, insoluble in petroleum ether, but readily soluble in ethyl ether.

The organic matter of McKittrite, viz., the portion soluble in chloroform, contains:—

Nitrogen	1·02 per cent.
Sulphur	2·50 „

Sample No. 4.—These pebbles were embedded in a black covering of elkerite. On scraping, the coating came off in flakes which appeared as transparent, irregular, yellow plates under the microscope. These plates were perfectly plain and showed no bubbly nor cellular appearance. They resembled thin plates of yellow glass, but were opaque to polarised light. Elkerite is soluble to a small extent in both acids and water, and slightly swells in the latter solvent. It is sparingly soluble in a solution of sodium hydroxide. Upon hydrolysis with hydrochloric acid the resultant liquors reduce Fehling solution and yield osazones, behaving like fucosite and algarite in this respect.

On heating, elkerite sinters and evolves water, oil, and gases, the latter possessing the smell of burnt feathers.

The Presence of Furfurol.—Furfurol has already been described as being one of the decomposition products of fucosite.

The Presence of Tertiary Amines and of Ammonium Salts.—These bodies appear during the hydrolysis of fucosite, elkerite and McKittrite. The methods employed for their detection are similar to those employed and described in the experiments demonstrating their appearance during the acid hydrolysis of the seaweed extract.

The Mineral Constituents of Oils and of the Bitumens herein described.—The methods employed in qualitatively examining the mineral constituents of the oils and bitumens described are similar to those employed and described at length in the case of the seaweed. The sands and clays were in the first place extracted with a mixture of nitric and hydrochloric acids,* as recommended by Moore, Parsons and others, in order to reduce the overburden of the large amounts of commonly occurring elements, such as silicon, iron, aluminium, calcium, magnesium, etc. Where possible the

* *Bureau of Mines Bull.*, 70. A Preliminary Report on Uranium, Radium and Vanadium, 1916; and *Bureau of Mines Bull.*, 174. Mineral Technology 12. Extraction and Recovery of Radium, Uranium and Vanadium from Carnotite, 1916.

pure oils and bitumens were ashed at a low temperature and the ashes examined without further treatment. The following tables give the results obtained :

Elements.	Sample 5. Oil ex sand by $CHCl_3$ extraction.	Sample 12. Oil ex wells.	Sample 4. Elkerite.
Aluminium	4+	a little	much
Antimony	0	0	0
Arsenic	0	3+	0
Barium	+	+	+
Beryllium	0	0	0
Bismuth	0	+	0
Boron	3+	0	3+
Cadmium	0	0	0
Cæsium	0	0	0
Calcium	3+	much	much
Chromium	3+	3+	6+
Cobalt	0	0	0
Germanium	0	0	0
Indium	+ (?)	0	0
Iron	a little	much	much
Lanthanum	0	0	0
Lead	2+	5+	+
Lithium	0	5+	2+
Magnesium	6+	5+	5+
Manganese	0	2+	2+
Molybdenum	3+	(?)	(?)
Nickel	0	much	2+
Niobium	0	0	0
Potassium	0	(?)	(?)
Rhubidium	+	0	3+
Silicon	4+	4+	much
Silver	0	0	0
Sodium	0 or +	much	much
Strontium	0	2+	+
Thallium	0	0	0
Tin	3+	much	0
Titanium	6+	0	4+
Vanadium	+	much	2+
Zinc	+	a little	0

Elements.	Sample 1. Fucosite scraped off the clay.	Sample 2. Fucosite ex sand, extr. by HNO_3.	Sample 6. McKittrite algarite.
Aluminium	much	much	much
Antimony	prob. absent	prob. absent	prob. absent
Arsenic	+	3+	0
Barium	+	4+	3+
Beryllium	0	0	0
Bismuth	0	0	0
Boron	6+	6+	5+
Cadmium	+	0	0
Cæsium	0	0	0
Calcium	much	much	a little
Chromium	a little	3+	a little
Cobalt	0	2+ (?)	0
Germanium	0	0	0
Indium	0	0	0
Iron	much	much	much
Lanthanum	0	0	0
Lead	+	+	3+
Lithium	4+	4+	4+
Magnesium	a little	much	a little
Manganese	2+	6—	2+
Molybdenum	prob. absent	prob. absent	prob. absent
Nickel	+ (?)	2+	6+
Niobium	0	0	0
Potassium	(?)	prob. absent	(?)
Rubidium	2+ (?)	(?)	(?)
Silicon	much	4+	much
Silver	0	0	0
Sodium	much	a little	a little
Strontium	+	4+	3+
Thallium	0	0	0
Tin	0	0	+
Titanium	6+	6+	5+
Vanadium	3+	3+	6+
Zinc	0	2+	3+

Experimental.

Section III.

The Conversion of Oil into Bodies Resembling the Fucose-Pentosans.

Crude oils from samples Nos. 12 and 13 were smeared on microscope slides and placed in an air oven at 110° C. for one month. Other slides were prepared in the same way and placed in a glass-

stoppered vessel provided with inlet and outlet tubes, through which coal gas could be passed on its way to the air-oven burner. After a period of one month it was found that those samples which were exposed to the atmosphere inside the air oven had become insoluble in chloroform, whilst those which were enveloped in the coal gas atmosphere were—like the original crude oil—still soluble in carbon disulphide and chloroform.

In a second experiment the fuel oil residues of samples Nos. 12 and 13 were prepared by distilling off the gasoline and kerosine fractions up to a temperature of 300° C. These residues were spread upon the slides in a similar manner, and heated in the air oven for one month. Similar slides were placed in the coal-gas atmosphere as above described. It was found that the resultant product was even insoluble in pyridine, and, of course, in carbon disulphide and chloroform, but there was no change in the solubility of the samples enclosed in the coal-gas atmosphere.

In another experiment carried out with the above fuel oil residues the oven temperature was maintained at 110° *F.*, so as to be comparable with the atmospheric temperatures obtaining in the Elk Hills. The product became insoluble in pyridine (comp. fucosite) and in chloroform (comp. algarite) after a period of nine months.

In another experiment the bituminous shale-like seep (sample No. 6) was subjected to a similar treatment. McKittrite is largely soluble in chloroform, but after heating for two weeks it became insoluble in chloroform. The chloroform extract of McKittrite, when subjected to similar treatment, became insoluble in pyridine after one month.

Preparation of Bulk Supply.—Fuel oil residues were heated at a temperature of 110° C. on sheet iron plates in a gas oven. Approximately 50 gms. of material were obtained. It was totally insoluble in chloroform, and 11 per cent. was insoluble in pyridine. The ash content was 0·31 per cent., and contained comparatively large quantities of the rarer elements.

Properties of "Pseudo-Fucosite."—The material is a black amorphous powder, when viewed in bulk; in the finely-ground condition it appeared to be brown, while in a thin layer on the microscope slide it appeared a yellowish-red by transmitted light. It is sparingly soluble in water and dilute acids, giving pale yellow solutions, possessing a neutral reaction in aqueous solution. It is soluble in dilute caustic soda solution. It is very sparingly soluble in ethyl and amyl alcohols, and is insoluble in most organic solvents with the exception of pyridine in which it may or may not dissolve according to the method of preparation, and the time during which it was subjected to the prolonged action of heat and the slow

oxidation process which takes place in the air oven. On heating it evolves oil, water, and gases smelling of burnt feathers; it sinters and swells at about 200° C.

After prolonged hydrolysis extending over a period of one week, with dilute sulphuric acid (5 per cent. by wt.) tungstic acid gave a precipitate with the tertiary amines formed during that operation. On the addition of a strong solution (33 per cent.) of caustic soda to the acid liquor, and boiling, the strongly alkaline solution gave off ammonia in very appreciable quantities.

The liquors readily reduced Fehling solution and formed osazones with phenyl hydrazine acetate.

On precipitating the free sulphuric acid with barium carbonate and filtering, the filtrate yielded a syrup upon evaporation. This syrup was sweet, but not very sweet, and in this respect it may be noted that arabinose is one of the least sweet of the sugars or pentoses. The syrup was redissolved in water and boiled with animal charcoal and refiltered. The colour of the concentrated filtrate was light yellow, and it deposited a small quantity of needle-shaped crystals, after standing for a few days. Under the microscope these appeared identical with those of arabinose. The liquors themselves readily gave an osazone, which, after recrystallisation from hot water melted at 156° C. M.P., arabinose osazone, 158–160° C.

A further quantity of 25 gms. of this pseudo-fucosite was hydrolysed for one week with sulphuric acid in a similar manner, and on extraction of the resultant solution with chloroform, 3·2 gms. of a light yellow oil were obtained, similar to that yielded by the seaweed extract.

Conclusions.

Algæ are partially soluble in boiling water, yielding alkaline solutions. These alkaline solutions contain sugars formed by the hydrolysis of the fucosan present in the algæ, and alkaline may be converted into gases by the action of anærobic bacteria.

Both bacterial action and oxidation, however, cause a change in the reaction of the alkaline solution, due to the formation of free sulphuric acid. At this stage the free sulphuric acid becomes the hydrolysing agent, and by its agency the fucosan is converted into sugars and the calcium salts of the ethereal sulphonic esters. The free sulphuric acid decomposes the sugars at low temperatures with the formation of algarite and an unstable variety of polyhydric fatty acids, which easily lose both their acidic radicle and part or whole of their oxygen, ultimately yielding hydrocarbon oils.

The calcium salts of the ethereal sulphonic esters are decomposed by water with the formation of mono-and di-hydric alcohols—free sulphuric acid and calcium sulphate. This continued formation of free sulphuric acid accelerates the hydrolytic process. As the esters disappear the tertiary amines make their appearance, and after this the ammonium salts are formed. These bodies are also unstable and readily yield oil which mixes with the mono- and di-hydric alcohols formed by the decomposition of the calcium sulphonic esters. The mixture of oils thus obtained contains naphthenic acids, organic sulphur and nitrogen compounds, traces of very many of the rarer elements and other decomposition products of the algæ. In fact, the mixture of oils possess the properties of naturally-occurring petroleum oils. The yield of oil and bitumen calculated on the water-soluble fraction of algæ is high, representing a minimum of 10 per cent. of oil and 43 per cent. of bitumen.

As the migration of underground waters is established, then it must be conceded that the soluble fractions of algæ, or the oil-forming substances, can also travel in aqueous solution from place to place. These solutions then decompose at leisure in some convenient geologic trap, whether this be on the original site of the deposition of the algæ, or at some distance therefrom. Upon decomposition such liquors precipitate algarite and calcium sulphate over the path of their travel, and at the same time oil is produced. It may happen that these occurrences are simultaneous, or it may be that the algarite and calcium sulphate are precipitated first and that the decomposition of the liquors is completed in another site.

In the case of McKittrite the algarite has been precipitated in bulk upon and in a diatomaceous earth, but in other cases it is possible that the algarite may be distributed throughout beds of an argillaceous nature. In the dried and metamorphosed condition such beds would be known as " shale " and the algarite as " Kerogen."

The Bitumens.—It appears that the view held at the present time that bitumen is an evolution product of oil must be modified in the light of the evidence now available. So far bitumen has been considered to have been derived from oil by such processes as concentration, polymerisation and oxidation. We now have evidence that bitumens exist, such as the fucosites and the algarites, which are capable of forming oil by degradation processes.

These processes have been described in detail and it has been shown that tertiary amines, ammonium salts, and sugars are formed as intermediate products, together with furfurol in smaller quantities. The major part of the sugars formed are pentoses, and arabinose predominates. We then have still another form of bitumen

in elkerite. This bitumen is made in nature by the slow oxidation of petroleum oil at very moderate temperatures under conditions which exist at the present day at the Elk Hills. This insoluble bitumen—a kerite— is deposited throughout certain sands, having been formed in the sands saturated with oil within living memory. Some of these sands are very acid, containing free sulphuric acid generated by the decomposition of the fucosites present, and this acid is capable of decomposing elkerite reforming the original type of oil.

Elkerite may be considered either as an oxidation product of oil, or as a body from which oil is produced by degradation. It has all the properties of a fucosite, it can be hydrolysed, and yields pentoses as intermediate products, and oil as one of the final products, thus exhibiting a fucosite-oil cycle.

Summary.

It has been shown that:—

(1) Oil and bitumen are products resultant upon the prolonged acid hydrolysis of algæ at low temperatures.

(2) Oil and bitumen can be produced by the acid hydrolysis of the decomposition products of algæ, *e.g.*, the sugars and the calcium salts of the ethereal sulphonic esters.

(3) By the acid hydrolysis of algæ a bitumen is produced—algarite—similar in properties to the naturally-occurring bitumen McKittrite.

(4) By the acid hydrolysis of sugar, a pure form of the above algarite is formed—algarose.

(5) Oils and bitumens are not formed by the alkaline hydrolysis of algæ.

(6) Some oils and bitumens contain the same range of metallic salts as algæ.

(7) Naturally-occurring oils and seepages contain the decomposition products of algæ in some instances.

(8) Some oils can be oxidised into fucosite, which upon hydrolysis yield sugars.

DISCUSSION.

The Chairman (Mr. J. McConnell Sanders) thanked the author for his very interesting and provocative paper. He seemed to have shown a direct relationship between carbo-hydrates and hydro-carbons. He had also added a few more words to our technological vocabulary. It was not quite fair to criticise in great detail a paper which had not been presented in full before the meeting, but in opening the discussion there were one or two points which he wished to bring forward as being of interest, and on which perhaps the author would be able to give further enlightenment.

Mr. Hackford had propounded some very revolutionary theories, and, because they were revolutionary, he was sure that Mr. Hackford would not only expect, but would welcome, a rather more critical attitude towards those theories than he would get if he had followed more conventional lines. As a general criticism of the paper, he would say that the author had been guilty rather of sins of omission than of commission. It was somewhat strange, for instance, to find so little reference to the classic work of Tollens and his collaborators on the hydrolysis of fucus, more particularly because those workers followed practically the same methods as that described by the author, although their results were entirely different.

Then the author had made no reference to the researches of Kylin on fucosan, which he regarded as the typical constituent of the bladders of the *fucoideæ*, and on *Lammarin*, which constituted a reserve foodstuff similar to starch, which was built up in the seaweed thallus in summer and utilised for growth and reproduction during winter. Considering that this substance, Lammarin, might constitute as much as 35 per cent. by weight of the seaweed, it should certainly have been considered. Kylin was also responsible for the statement that all the *fucoideæ* and *florideæ* contained nitrogen as ammonia and that some contained it as nitrate.

He noticed that the author had rather stressed the importance of the mineral constituents of seaweeds as evidence of their similarity to the oils and bitumens. He could not help feeling that the analogy might be somewhat overstrained. It was well known that in marine Algæ there was a certain biological succession in the mineral substances which they assimilated, not only in amount, but also as regards the actual nature of the elements utilised by the plant during its life. For instance, Sargassum contained its maximum of Iodine in the spring, when maturation commenced, and its minimum in autumn. Calcium, magnesium, potassium, sodium, silicon and chlorine gradually increased in quantity during the formation of spores, while after sporulation those elements decreased in amount. Then again, with the *fucoideæ*, phosphorus is present in the young parts of the thallus, but not in the older

portions. Hence the expressions "much" or "little" or "probably absent" in the comparative table given by the author had really not quite the importance that the author seemed to attach to them. He had little doubt that a spectroscopic examination of a fragment of drift wood from the Brighton foreshore would reveal practically all the elements recorded by Mr. Hackford, but he would hestitate to connect that circumstance with the origin of oil. This was rather stretching the analogy farther than it should be stressed, but it was the idea he had in his mind.

The author spoke of a naturally occurring material which he had baptised Fucosite, and recorded that this was identified by Prof. Tabor as a blue-green alga. This identification seemed to him (the speaker) of extreme importance, because the *cyanophycæa* belonged to a distinct class of algæ from those referred to by the author in the earlier part of his paper. They were known to form masses on damp walls or even on damp ground; they were usually terrestrial rather than marine, and it was quite likely that the material found by Mr. Hackford in the natural seepages were of far more recent origin than the oils or bitumen, and indeed might have no connection with either oil or seaweed. Anyway, it would have seemed more logical to have made his comparative experiments on algal hydrolysis with a representative specimen of blue-green alga, instead of *laminaria* from Brighton.

This brought him to another point which he hoped the author would be able to clear up. In his experiments with the Brighton seaweed he referred to the production of a substance which he said was oil, containing 21.8 per cent. of naphthenic acids and 78.2 per cent. of hydrocarbons. Of course, no one knew better than Mr. Hackford what petroleum oil looked like, and if he looked at a bituminous substance and called it McKittrite it might be taken that he knew what he was talking about; but, for the benefit of those subsequent readers who might not be aware of Mr. Hackford's ability in tracking down hydrocarbon oils to their birthplace it would be useful to include the actual chemical evidence that the products were hydrocarbons and naphthenic acids, since all that was actually stated was that the product was in part soluble in caustic soda and partly stable to sulphuric acid. Pure furfuraldehyde dissolved in cold concentrated sulphuric acid unaltered and without turning brown, and in its commercial preparation it was known that the crude material was liable to contain an oily compound of much higher boiling-point. This was of interest because, as shown by Tollens and Muther, Carragheen moss on hydrolysis with dilute sulphuric acid gave methyl furfuraldehyde, which was known to be the intermediate product in the hydrolysis of fructose to laevulic acid.

After all, was there any need of the explanation adduced by Mr. Hackford ? The theory that marine algæ might have been one of the sources of petroleum was by no means new. Marcusson, in 1925, showed that fats from algæ resembled those from marine animals. The objection due to Porter, and mentioned in the paper, to the Engler-Höfer theory, that the gases obtained from the distillation of Menhaden oil contained carbon monoxide and olefines was not really an objection, since Kraemer and Spilker had shown that the waxes obtained from algæ gave these gases on distillation also. The brown algæ contained oil naturally, and, as shown by Tsigimoto, *Lammaria* and Sargassum contained also highly unsaturated fatty acids. The fossil algæ *Reinschia* found in the Carboniferous and Permian was almost identical in the form of its cell colonies with *Botryococcus coorongia*, which stored up oil in its cells, and the masses of tough bituminous matter which the latter forms were almost certainly derived from that naturally secreted oil. Therefore, one wondered if it was necessary to go to the somewhat elaborate chemical theory to account for oil if the plant was already storing it up. All that was required really was to prove that that oil eventually ended up as hydrocarbon.

He was much interested in the materials which Mr. Hackford called Elkerite and Fucosite, since this corroborated some researches which he (the speaker) had been carrying out, the results of which he hoped to place before the Institution at an early date.

As a matter of interest in this connection, he might mention that tragacanth gum, which, as was well known, came from a terrestrial leguminous plant, according to Tollens yielded fucose and arabinose by hydrolysis, while one variety also gave xylose. Hence, if oil could be obtained from fucose by hydrolysis, it could also be obtained from tragacanth, and therefore was just as likely to be terrestrial in orgin as marine. In passing, one wondered whether the property of swelling with water, ascribed to fucosite, might not have some relation to the similar propery possessed by tragacanth. Of equal interest was the fact mentioned by Dr. Otto Rahn, that a mould-fungus existed which could decompose paraffin wax to the extent of 77 to 79 per cent. in six weeks.

Dr. A. Wade said that it was not so much what the author said in the paper as what the discoveries involved might lead to, the other researches which might be founded on it. Other people would take the work in hand, no doubt, both in England, on the Continent, and in the United States, and would probably build up a number of researches which would be of the greatest importance to the petroleum industry.

One thing which had struck him as of particular importance in the paper was the way in which the author indicated not only the

building up of petroleum from the algæ, but the reverse process. He had performed the whole cycle of operations, beginning with one simple element and producing oil, and then going right away back to the sugars, fucosite and so forth. In the course of that cycle of operations there were numerous points which might very well form the foundation for a number of very important researches not only on the purely scientific side, but having great economic possibilities.

He supposed that all members understood from the paper that the author was dealing with the formation of petroleum in only one of its aspects, that based on derivation from the algæ. He did not think the author meant to exclude other sources from which petroleum might be formed. The author had based his work upon the algæ, but he had not claimed that many other substances, such as those referred to by the Chairman, could not be taken as bases for similar pieces of research. The paper did not mean that all kinds of petroleums necessarily originated from the algæ, but there might be many other sources of origin, marine or terrestrial, from which, perhaps, the same or a similar cycle of events could be traced.

The paper particularly interested him because in 1913 he had conceived the idea of doing both chemical and microscopic research upon the black muds which covered the coral reefs in the Red Sea area. It was not an original idea, for Fraas and others had already tackled the same problem ; but he thought that perhaps it might be useful to begin again and see what could be got out of it. In the course of the work some rather interesting results had emerged. These black muds were almost invariably covered by sea water, so that their organic contents were decomposing under anerobic conditions. When he started to examine them under the microscope, he found not only certain microscopic bodies which resembled bacteria, but certain granular bodies which eventually, by straining and in other ways, he thought he had identified as starch. Petroleum of a pale straw colour was isolated. It was what he thought Mr. Hackford would call a juvenile petroleum, and in association with it starch and nitrogenous matter had been found. At that stage he had written up the results of the work as far as it had gone, but unfortunately he had had to proceed to Australia. The work was left as it stood in the hands of S. R. Illingworth, who had finally published a paper in the *Mining Magazine* of August, 1914, on the "Origin of Petroleum." To his astonishment, he found that Illingworth, in his further chemical examination, had not found evidence of starch being present, although he had been a collaborator and had gone through the tests which had satisfied them at the time. What happened in the ensuing period and where the samples got to he did not know, so he did not quite know what to make of the

final form of the paper; but, at any rate, if starch was present—starch, of course, was closely allied to sugar—it would have been of very great importance. Recent work had been done on similar muds, but he felt that there was room for further research on these lines, which should now be especially stimulated by the methods used and in the light thrown upon the subject by Mr. Hackford's interesting paper.

Prof. Nash, in a written contribution, said : In dealing with the nature and origin of the organic material in boghead coal and similar material capable of yielding petroleum-like oil on distillation at high temperatures, a number of investigators have produced evidence of the algæ theory, and descriptions of the blue-green and green algæ of the many genera concerned are given in the literature.

Of these may be quoted David (*Linnean Soc. N.S.W. Proc.*, 1889, **4**, p.p. 483–500), who announced this view after exhaustive researches on Australian torbanite, and Bertrand and Renault (*Soc. Ind. Min. St. Etienne Bull.*, 1899, **13**, pp. 895–1191), who advanced the theory that the organic matter of torbanite is derived, in the main, from microscopic gelatinous algæ of different species.

Thiessen (*Origin of the Boghead Coals, U.S. Geol. Surv. Paper*, 1925, **132**, p. 133) describes the yellow bodies found in torbanites as colonies of alga-like organisms, similar to organisms now living in the salt lagoons of South Australia. Colonies of these collect on the lake shores to form a rubber-like mass known as Coorongite, which, in Thiessen's view, corresponds to the peat stage of boghead coal.

Petrie (*J.S.C.I.*, 1905, **24**, p. 997) refers to the extraction from torbanite by solvents, of a reddish brown viscous substance with a dark green fluorescence by reflected light, which, when heated to 160° C., began to volatilise and blackened, and on cooling set to a tough, rubber-like, odourless solid of dark brown colour. It is probable, therefore, that the many types of algal remains to be found may be made to yield bitumen and oil, having similar properties, when subjected to varying conditions of temperature in a retort.

The author appears to have neglected the important part which micro-organisms play in the slow decomposition of organic matter. Undoubtedly varied products of decomposition can be formed from the same parent material by the action of different micro-organisms. Again, have we justification for assuming that petroleum is derived from algæ because the sugar from marine algæ may be converted to algarite by hydrolysis, a certain oil may be oxidised to fucose pentosan, and fucose pentosan may be hydrolysed to sugars ?

The author has made out a very strong case for the conversion of algæ into a *certain type of bitumen*, but his theory that bitumen is an intermediate step in the generation of petroleum is not so convincing.

The statement that a Californian bitumen was largely soluble in 1 per cent. soda solution, and that on hydrolysis the solution contained the pentose arabinose, is most important evidence in connection with the author's theory; also, the similarity in behaviour of fucosite and the bitumens under investigation is most convincing. However, has the author treated any other bitumen with a 1 per cent. soda solution so that this property may be generalised?

One could only wish for more evidence upon the relation of these bitumens to natural petroleum oils in general. Bitumens usually need hydrogenation under elevated temperature and pressure to yield oils of similar nature to petroleum. The presence of sugars and ammonium salts in well waters and of carbon dioxide in natural gases would not be accepted as sufficient evidence by many.

The fact that algæ contain the same range of metallic salts as some oils and bitumens is difficult to accept as proof of the algal origin of these particular oils and bitumens, because it is a well-known biological fact that algæ will adapt themselves to varying conditions. The author himself states, "algae are plants which absorb their mineral constituents by their whole surface from the waters in which they live." Petroleum is invariably found in proximity to salt water, which in some instances is considered to be connate water, and would thus contain similar metallic salts as those absorbed by algæ.

Geologists would be the first to draw attention to the improbability of many deposits being made up of one class of organic remains only—*e.g.*, algæ. Coal, torbanite, oil shale, etc., may be taken as examples of deposits of mixed character. The author has very ably presented facts to prove that certain bitumens owe their origin largely to algæ, yet sufficient evidence has in the past been put forward to suggest that some oils may owe their origin to fish and other lower animal organisms. It would be hard to imagine large algæ deposits without animal deposits also, and the relative proportions of the parent material would doubtless affect the nature of the oils produced on decomposition, apart from any effect which micro-organisms might have.

Although Mr. Hackford has explained the origin of certain bitumens from algæ, we must not disregard the animal origin theory entirely.

A valuable link in the chain of evidence for the carbohydrate theory of the origin of petroleum would be the discovery of oil deposits in the various stages of development from the bitumen, as suggested by the author.

Dr. P. Haas said he was inclined to agree with the Chairman in most of the remarks he had made, that a very great number of extremely contentious, not to say provocative, claims had been made, and he could not help feeling that a great many of the statements made were certainly made with insufficient evidence and proof. He was very interested and pleased to see that Mr. Hackford was taking up such a subject, but he was not prepared to agree with his results.

Of course, with regard to the question of the algal origin or otherwise of seaweeds and any question in regard to petroleum and bitumen, he was not prepared to cross swords with Mr. Hackford, but, when it came to the purely chemical side of the question, he must say he would like a good deal more evidence in support of the many intriguing suggestions contained in the paper.

Dr. P. E. Spielmann said that one often saw papers which described observations made in the laboratory from which theories on the production of oil were made with a certain amount of strain ; but in the present instance the author had got so much evidence from the oil itself, linked up with his subsequent laboratory substantiations, that for him, at any rate, it carried very great weight in its main principles, even though there were certain points of chemistry that had not been actually brought before the meeting. The author, in the future work which he contemplated, would probably clinch these matters, and would prove, without any doubt, that algæ did form a source of the origin of petroleum. He hoped that Mr. Hackford would carry out analogous work on the other great organic substance that was supposed to give oil—namely, fish.

The following written contribution was subsequently received from **Mr. A. Beeby Thompson** :—

As a purely chemical paper, it is difficult for others than chemists to contribute any pertinent comments, but a fuller description of the mode of occurrence of the products examined would, it is submitted, enhance the value of the contribution. The paper does not enable one to judge of the geological relationship of the samples examined to the general geology.

The author spoke of the impregnated material as covering 7 to 8 square miles, but does not make it clear where this is or whether this deposit is part of the Tertiary series, recent surface drift, or material ejected from some vast mud volcano or volcanos.

The large dyke of solid bitumen (McKittrite) referred to as being exposed for more than 1000 ft. up the side of a cliff would appear to be one of the typical veins found in the complex and faulted structures of these San Joachin Valley fields, and its age is likely to be very antecedent to the live seepages described a few lines

later in the paper. Bitumen from veins generally possesses quite different properties to seepage masses of more recent origin, and direct present-day connection with liquid oil can rarely be traced.

We have abundant proof that very complex reactions occur along the outcrops of oil-bearing strata in desiccated regions where there is insufficient rainfall to wash away efflorescences and incrustations. Some of the most striking in beauty and extent are to be found in the Peruvian oilfields, where brilliant-coloured crystalline salts can be uncovered by raising slabs of incrusted material with a mushroom-like growth overlying the oil rocks in low and sheltered spots. In some respects it is to be regretted that so important a research should have been restricted to material from an oilfield where the geological conditions are distinctly unusual. The upper oils which occur near the unconformable junction of the Etchegoin and Maricopa are particularly heavy and may be secondary in origin; indeed, their high density 0.959 to 0.979 suggests migration, especially as 0.947 gravity oil is found in sand lenticles of the underlying Maricopa shale series.

The remark by the author that the impregnated sands cover some seven to eight square miles suggests that the deposit is abnormal and that the material is associated with some curious local circumstances. Perhaps the author could elucidate the situation by a brief description of the geological conditions.

Mr. J. E. Hackford (in reply) thanked the Chairman for his carefully considered remarks. He said he was aware of the work of Tollens and Kylin, and knew their results differed from his own in many respects because, he thought, the problem had been attacked from entirely different angles. This was the reason he had relied so much on the work of Haas, who had not only shown the modus operandi of the formation of free sulphuric acid for the subsequent continuous acid hydrolysis of the algæ, but had also recorded the formation of algarite. It is true this formation had been no more than noted, but, nevertheless, it was in his opinion a distinct advance and a discovery of such importance that it justified him in quoting Haas rather than Tollens and Kylin. It was impossible to quote and do justice to the numerous workers in this field.

With regard to the Chairman's criticism that the analogy of the mineral constituents of seaweeds and bitumens had been somewhat overstressed, he would remark that he had endeavoured not to overstress this point, and had therefore omitted reference to the same in both the "Summary" and "Conclusions" of the paper. That the similarity was there was all to the good, but, had the metals been dissimilar, then it would be apparent that other reasons than those he had advanced would have to account for the similarity and relationship existing between algæ and bitumens.

He agreed with the Chairman that the workers he (the Chairman) had mentioned had ascertained the presence of fats, fatty acids, etc., in both diatoms, seaweeds, etc. This fact was well known, but he referred the chairman to Thrask and Hammer's views as recorded on page 80 of the paper in which he had emphasised that point. Dealing with the action of bacteria upon such bodies, the following sentence had been put in italics: "Some anaerobic bacteria form methane, but none is known to generate hydrocarbons that characterise petroleum."

One of the chief aims of his paper had been to show that oils having the characteristics of petroleum oils could be produced from algæ by simple methods such as could be reproduced in nature.

In reply to Prof. Nash, he felt that the remark that he had neglected the action of micro-organisms in the slow decomposition of organic matter was hardly justified. The importance of Taylor's work on the bacterial decomposition of organic matter under alkaline conditions had been stressed, and the author has had some correspondence on this subject with Dr. Taylor. In addition, the evidence of Thrask, Hammer and White had been quoted. Experiments were quoted to show that bacterial action (inter alia) changed the alkaline algal extracts to ones having an acid reaction. The major part of this research commenced at this point, and care had been taken to show how these acid solutions were obtained.

He also stated that he had emphasised the fact that he had not disregarded the possibility of oils having origins from animal or other sources, attention here being drawn to the definition of "Protobitumen."

Although outside the scope of this paper, he would like to advise Prof. Nash that sugars could be obtained by similar processes from some shales and coal. With regard to the Bergius process, the reduction of bitumen can be the more readily understood if it be considered as a modification of Kiliani's method of reducing an hydroxyl group by means of hydriodic acid. He thought Prof. Nash had drawn attention to points that would prove of general interest, and thanked him for his remarks.

With regard to Dr. Haas's remarks on the chemical evidence, many of the statements he had made—he thought, without exception, all of them—had been taken verbatim from Dr. Haas's writings. The acknowledgments due to him were more numerous than to any other author quoted in his (the author's) paper.

He thanked both Drs. Wade and Spielmann for their kind remarks.

In reply to Mr. Beeby Thompson, he did not feel that he could do justice to the written criticism and request for details on the geological conditions at site of the bitumens and oils examined, but he had no doubt that authentic information will shortly be published.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

FIRST DINNER OF THE TRINIDAD BRANCH.

THE FIRST DINNER of the Trinidad Branch of the Institution of Petroleum Technologists was held at the Queen's Park Hotel, Port-of-Spain, on Saturday, October 24, 1931, Mr. A. F. Dabell, M.I.Mech.E., Member of Council, in the Chair. The principal guest of the evening was the Governor, His Excellency, Sir Claud Hollis, K.C.M.G., C.B.E., who was attended by his A.D.C., Mr. A. J. de Boissiere. The following members and guests were also present :—

Messrs. H. A. Bennett, N. Betancourt, E. C. Buck, L. A. Bushe, C. E. Capito, O.B.E., Hon. A. P. Catherall, A. Chadwick, R. R. Chenault, H. S. Conder, W. J. C. Cooke, C. L. Cowen, A. J. Creswell, F. W. Creswell, B. W. Deane, L. A. A. de Verteuil, W. de Verteuil, N. W. Dyer, G. Evans, C.I.E., S. E. Falkes, H. D. Fletcher, A. Gordon, N. W. Graham, Hon. Fred G. Grant, Dr. G. R. Gribben, M. Hamel-Smith, H. A. Harris, J. L. Harris, M.C., Lt.-Col. the Hon. H. C. B. Hickling, D.S.O., M.C., J. D. Hobson, L. L. Kennedy, R. N. Kirby, Dr. H. G. Kugler, L. Kummer, Commdr. H. V. Lavington, J. F. Leary, T. P. Little, G. Mardall, J. W. Macgillivray, E. J. Marsden, N. Matheson, A. Mathews, A. R. McLean, F. Middleton, E. L. Moore, Hon. M. A. Murphy, C.B.E., M. A. K. Murray, O. Nothnagel, B. Novikoff, Hon. L. A. P. O'Reilly, K.C., A. L. Owens, A. L. Payne, Capt. A. F. C. Peters, M.C., D.C.M., J. P. Potter, D. W. Ramsey, H. W. Reid, A. H. Richard, Rev. J. Robinson, E. G. Rooks, E. C. Scott, M.C., G. H. Scott, G. H. Simpson, M.B.E., A. W. Slatter, A. G. Tanner, D.S.O., M.C., H. C. H. Thomas, F. H. L. Tindall, L. A. Toone, C. L. Vandeburgh, D. M. Walsh, C. C. Wilson, L. J. Wilson, E. Zurcher.

"The King."

The toast of "The King," proposed by the Chairman, was loyally honoured.

"The Institution of Petroleum Technologists."

His Excellency the Governor, in proposing the toast of "The Institution of Petroleum Technologists," said :—

To me has been entrusted what may indeed be claimed to be the toast of the evening, for it is the toast of the Institution of Petroleum Technologists, and it is therefore my privilege and duty, however ignorant of the subject I may be, to tell those members present something about themselves.

The subject may be described as a gassy one, but I shall endeavour to be brief, and I shall keep in mind the saying: "If you don't strike oil quickly, stop boring."

Now, having been entrusted with this important toast, I feel that I must not be flippant, but before I become really serious I should like to confess that when I was asked to propose the toast of the Institution the thought flashed through my mind that the occasion was one which George Morrow might well have immortalised in his series of drawings in "Punch" entitled "Entertainments at which we have never assisted."

I am happy to say, gentlemen, that I am not as ignorant of the subject as I might have been had I not had the good fortune to meet last year in London, first, Mr. Southwell, who had recently returned from Trinidad, and then Mr. Capito, who was on his way here; for I took the opportunity to inquire at the Colonial Office what a Petroleum Technologist exactly is. The reply came promptly, almost contemptuously: "A Petroleum Technologist is a geologist, a chemist, a civil engineer, a mechanical engineer and a mining engineer." That so many professions or qualifications could be combined in one person nearly took my breath away, and, being of an inquisitive nature, I made further inquiries. I then learnt that the Institution of Petroleum Technologists had its inception in the realisation of the need of some means of bringing into contact and co-operation engineers, geologists, chemists, financiers, and experts in transportation and commerce; in short, men who are engaged in the several branches of their respective professions which are specially connected with petroleum.

We British are at once the most clubbable and the most centrifugal of peoples, and whenever two or more of us are gathered together we invariably form a club, a society or an institution.

In 1913, twenty-nine leading spirits in the petroleum world agreed to form a corporate institution with a view to amalgamating the diverse constituents which I have mentioned, and this was how the Institution of Petroleum Technologists was founded.

From this small beginning the Institution has become, in less than 20 years, world-wide in its activities, cosmopolitan in its membership, and comprehensive in the whole of the science and technology of the subject.

I do not propose to comment upon these days of stress and competition through which we are passing, when the oil industry in Trinidad is fighting for its very existence, but I venture to remind you of the saying: "Fire is the test of gold, and adversity is the test of strong men."

It is in difficult times such as you are now experiencing that the true value to the oil companies of the services of Petroleum Technologists becomes apparent.

The Institution of Petroleum Technologists held its first dinner in 1918, and of late years, the branches in Persia and Rumania have held annual dinners at about the same time as the parent society. Trinidad Branch has now decided to follow suit. I offer its members my congratulations and my thanks for inviting me to be present at this their first dinner, which I hope may become an annual event.

I now ask you to drink to the Institution, coupled with the name of your Chairman.

The Chairman (Mr. A. Frank Dabell), in responding to the toast of "The Institution of Petroleum Technologists," said :—

I am honoured by being entrusted this evening to reply to the toast of "The Institution of Petroleum Technologists."

Last year at the annual dinner of the Institution in London, our distinguished President, Dr. A. E. Dunstan, in replying to this toast, took for his text the words of Plato, "The aim of a veritable community is not that this or that person should prosper, but that the whole should flourish."

Those who attend our meetings regularly will appreciate that, purposely or otherwise, we do endeavour to attain this ideal, for no individual gains material benefit by his presence at the meetings where, at the most, whoever can, teaches, and whoever will, learns.

The Trinidad Branch has been in active existence for four years, during which time some 30 papers have been read and discussed by members and visitors, varying in number from 20 to 50, each of whom, it is to be appreciated, is an active unit in the industry.

Most of those attending have some knowledge of all branches of the industry and an intimate specialised knowledge of one, and, in consequence, service of an ever-increasing value to the industry accrues.

The idea of the present gathering originated with a remark made by an official of the Anglo-Persian that it was our duty in this time of depression to keep the flag flying. I think I am right in assuming that this same reason prompts His Excellency in honouring us with his presence this evening.

It may be argued that, as Petroleum Technologists, we should find joy in the situation of the oil industry to-day, in that, as a result of the efforts of this and kindred bodies an ever-increasing demand for a world requirement—petroleum—is being satisfied with decreasing labour, thereby leaving more time for ease and study on the part of the members.

Some of our absent members having the time for ease and study would, I feel sure, retort that there are other essential factors which call for consideration.

Certain it is that during the past few years technologists have done their duties so well in the introduction and development of new methods of geological survey, drilling, producing and refining, that an increased output is being obtained with reduced effort.

Wells can be drilled to-day in one-third of the time they would have taken ten years ago, and at the same time more precise information obtained as to the formations passed through and the verticality of the hole. The 10,000 ft. well which was yesterday regarded as an impossibility is to-day a reality.

Applied to Trinidad, fields are now being advantageously developed from which it would have been impossible to obtain commercial production with the best known practice of even five years ago. Taking one example only, it is now possible, by the use of the modern barytes method of controlling high pressures to bring into production simultaneously a whole series of producing sands which, developed separately, carry no commercial value.

As a result of our efforts, crude petroleum is now being brought to the surface faster than it can be absorbed in industry. Whilst, strictly speaking, it is not the duty of the technologist to forward proposals to remedy this trouble, we can say that the conservation of resources, by co-operative means or otherwise, must fail unless unnecessary and uneconomic drilling be treated in like manner, for petroleum should remain in its natural reservoir, the earth, until it is required.

Trinidad, with an output of less than 1 per cent. of the world supply, is of small moment in the world market, but the words of Plato apply with equal force to individuals or nations.

The Institution and the Industry being inter-dependent, a further result of our efforts has been to throw out of employment a large number of our members which, in itself, is sufficiently regrettable, but it has entailed a great reduction in the number of manual labourers employed and also a reduction in the wage rates of such as remain in employment.

Under so-called normal conditions, the law of supply and demand in operation resulted in excess labour in one industry being deflected to another, but, unfortunately, to-day, all industries would appear to be in a similar position to that of our own, from which is to be seen the anomaly that, when the world required less, the winning gave employment to, and supported, all.

Incidentally, I was told some years ago by a super-salesman extolling the importance of his profession that : " Any fool could produce, but to sell, brains were needed." It would seem that the fool has advanced more rapidly than the man of brains.

Expressed technically, the output of the world is governed by the man-hour effort, that is, the produce of the number of men and the hours of their employment.

Remedy for excess production is to-day being sought by a reduction in the main factor; but is it beyond the wit of economists to evolve a system by which improvement in technique leaves the same number of men in employment by reducing the number of hours worked?

In fact, this is being done in a small way in Trinidad to-day, but, unfortunately, applied only to manual labour.

I venture to suggest that, under average conditions, if 20 members of the skilled or unskilled class were asked to forgo 5 per cent. of their salary in order to maintain in employment a colleague of good character, they would readily do so, and it may be that in development of this principle assistance will be found for the less fortunate.

It is only fair to mention that, upon a recent occasion, I advanced to a smaller, youthful and more intimate body of friends the suggestion that all men in the industry over 50 years of age should retire from active service. This was received with the correct signs of conventional sympathy befitting my assumed retirement, but a further suggestion that those remaining in service should allocate 50 per cent. of their salaries for the maintenance of those retiring was received with a manifest lack of enthusiasm.

However, if, after the manner of Robinson Crusoe, the Petroleum Technologists working in Trinidad will draw up a balance-sheet of the advantages and disadvantages of service in this Island, I am certain it will be found that the former overwhelmingly predominate, and that an item of outstanding importance on the credit side is represented by the Government.

Speaking from a varied experience of countries and conditions, I am glad to have the opportunity of declaring that the Government of Trinidad is the nearest approach to perfection that it has been my fortune to work under.

To those who think otherwise, either by reason of familiarity or Irish origin, I shall be pleased to give a few addresses where, I am certain, after short residence, my statement will be cordially confirmed.

It is my duty to advise fellow members this evening that the bulk of the work called for by, and culminating in, this meeting has been carried out by our honorary Secretary, Mr. Reid, to whom our thanks are due.

On behalf of the Institution of Petroleum Technologists, I thank Your Excellency for having honoured us by attending our dinner and for the enthusiastic manner in which you proposed the toast.

It is our hope that, collectively and individually, we shall prove deserving of your good wishes.

"The Industries of Trinidad."

Lt.-Col. the Hon. H. C. B. Hickling in proposing the toast, "The Industries of Trinidad," said:—

When informed by your Chairman last week, before I had even got off the boat, of the honourable duty allotted to me this evening, I looked up the definition of the word "Industry" and found it given as "Habitual diligence in any employment." Having decided to study my subject at first hand, I proceeded forthwith to the Union Club to write to your Secretary declining the honour. However, I found a second definition, which read as follows: "Productive occupation," and I breathed again, because I could treat that subject without being libellous.

The industries of the Colony in no way differ from those of the world which are to-day passing through great difficulties, and although the part played by industry in the causation of these difficulties is not that of the "villain of the piece," yet undoubtedly it is a very important one.

Primitive man had many good points, but he was a "Jack of all trades"; he had to be, and could make but very poor use of human effort. Industry, however, very soon got busy and started specialisation. This multiplied the produce of human effort considerably, and when the forces of nature were enlisted the multiplicative effort had to be measured by the thousand fold, with the result that in present circumstances there is a superfluity of almost every known product—except, possibly, limes, and that, gentlemen, is a ghastly thought—and that is the position, although there are 20,000,000 of unemployed in Europe and the United States. An outstanding example of the multiplicative effort is the "tin lizzie." You can buy that car at a price which represents a good deal less money than that paid for 40 days work for one man, and that includes the production of the raw product and the manufacture right through to the finished article. I wonder how long primitive man would have taken to make a "tin lizzie"; probably two or three lifetimes.

How simple industry was in earlier days when there was almost biblical authority for the merit attached to those who grew two blades of grass where one grew formerly. To-day it is very different. We hear of the most prominent citizens in the Southern States of America suggesting that, in order to prevent over-production, every third row of growing cotton should be ploughed under. Certainly, if we adopted that remedy, it would be a horrible indictment of the system under which we work. It almost

appears to me that the time has come for those responsible for the stupendous increase in productive power to switch their thoughts from production to consumption, and so improve distribution and exchange that an improved power of consumption will catch up and keep pace with future improvements in production.

Primitive man was really a long way ahead of us in this. It is axiomatic that Adam's consumption was always up to his production. He usually went to bed hungry. Eve also was a long way ahead. She was the person who originated the loose leaf system.

Modern invention and industry are in effect continuously reducing the world in size. We are all so close to one another that community of interest is increasing rapidly, and one can almost paraphrase Lincoln and say, " this world cannot exist half-sick and half-well." Industry appears to have found this out already, as there is a distinct international trend in those industries that are more advanced, and the world may find it advisable to follow suit.

Gentlemen, the time is getting on, and I always remember the advice to after-dinner speakers given by the greatest of all Englishmen, you remember, Macbeth, " If it were done, when 'tis done, then t'were well it were done quickly," and I, therefore, give you the toast, " The Industries of Trinidad," and may they work unitedly and pull through successfully.

The Hon. Fred. G. Grant in responding to the toast, " The Industries of Trinidad," said :—

It is my privilege and pleasure, as Acting-President of the Trinidad Chamber of Commerce, to reply to the important toast, " The Industries of Trinidad," so ably proposed by my friend, Colonel Hickling. I am sure, Mr. Chairman, that everyone interested in Trinidad will appreciate your action in including " The Industries of Trinidad" in the toast list of this, your first, annual dinner.

It has been suggested that Trinidad, by virtue of its situation, size and population, is chiefly concerned in the production of primary products. A new outlook has, however, appeared during the past few years, and the thinking men of this community are considering ways and means of developing local industries which would be profitable to investors, furnish desirable and remunerative employment and generally benefit this Island and its people.

The oilfields have, of course, been responsible for our chief industrial development. Not many years ago, the oil industry could almost be listed under the heading of primary products. Subsequently, the refining end of the business was developed, and to-day we have a number of major and minor oil products, formerly imported, but now available not only for Trinidad, but also for outside points in suitable qualities and at competitive prices.

Most of you around this table are very much better acquainted with the development of the oil and asphalt industries than myself, and I shall, therefore, confine my remarks to the industrial development of Trinidad in other directions.

I do not for one moment suggest that industries should be developed indiscriminately and without due regard to their ultimate benefit to the community, and consideration must naturally be given to the scope and economic value of each. We have, however, many examples of local industries which have been profitably developed with reasonable protection and with benefit to our Island's revenue, employment and the public generally.

The development of local industries will be of particular benefit to artisans, of whom we have a large number, increased by the return of many of these men from Maracaibo, who cannot now obtain employment due to the unfavourable conditions with which our oil, asphalt and other industries are faced.

We should and must find suitable employment for this class of labour, and, as far as I can see, this can only be accomplished by a revival in the existing industries and the development of new ones. Apart from the artisan class, there are a number of educated young men in Trinidad to-day for whom avenues of employment should be opened, and to whom the industrial development of Trinidad would offer suitable opportunities and remunerative employment.

On account of our oil and asphalt industries, we are able to welcome to our midst men like yourselves, specially trained to investigate and develop industrial undertakings. It is true that you are here in connection with a specific industry, but your training and your organising ability would be of inestimable value to us in the investigation and development of others.

I am sure that the people of Trinidad are glad to have you, and, like yourselves, sincerely hope for the early revival of the oil industry. I do earnestly ask you, during your stay in Trinidad, to take an interest in our affairs, assist us in the development of new industries and generally give us the benefit of your training and organising ability, to help the development to which I have referred. Our Government recognise the need for industrial development. Our business men are considering the question carefully, and all of us, I can assure you, would welcome and appreciate your assistance as trained investigators and trained organisers in the development of the industries of Trinidad.

"Our Guests."

Mr. C. Erik Capito, O.B.E., in proposing the toast of "Our Guests," said: We are indeed honoured by the presence of His Excellency Sir Claude Hollis. The Governor is probably the busiest

man in the Island, and is continually being called on to make speeches, sometimes at very short notice, and we all very much appreciate that he has spared us time to come here and propose the toast of our Institution in such a kind manner.

In Mr. Murphy we have the *doyen* of the Engineering Profession in the Colony. The excellence of our Public and Private Engineering show that we are keeping well abreast of development elsewhere.

We are also fortunate in having with us Mr. Fred Grant, a Past-President and present Vice-President of the Chamber of Commerce. Commerce is also represented by several gentlemen, including Mr. Edgar Marsden and Mr. Wilfrid de Verteuil.

As representing Law, we have with us Messrs. L. A. P. O'Reilly, J. D. Hobson and Michael Hamel-Smith. I am sure from the eminence these gentlemen have attained in their profession that they have rigidly adhered to the good resolutions made by the Lord Chancellor in "Iolanthe."

The Church is represented here by Mr. Robinson, the Chaplain to the Oil Companies. In this connection I noticed the other day that Mr. Clayton, the Chaplain to Toc H., has been appointed Chaplain to the Anglo-Persian Oil Company. There is no doubt that the Church has other spheres of action than marrying and burying us. An energetic padre can do a lot to help the management of an oilfield in promoting healthy social and sporting movements, more especially amongst the less senior members of the staff.

We are very pleased to have Dr. Gribben here to-night as representing Medicine. His *confrères*, whom we had also hoped to be with us, have, for one reason of another, not been able to come.

In Mr. Geoffrey Evans, the Principal of the Imperial College of Tropical Agriculture, we have both Science and Agriculture represented.

I think our scientific teachers, as a whole, have been set a problem. As mentioned by Colonel Hickling, up to comparatively recently, we have always been taught that if we could produce two where we previously obtained one, we were well on the way to prosperity. Nowadays this does not appear to be true, as we are getting less money for two than we were getting for one. As international economics are not my strong point, I must leave the problem to be dealt with by others.

Lastly, but by no means least, we welcome to our board the General Manager or Acting General Manager of every oil company in the Island, together with most of the senior members of the oil companies' staffs. We hope that many of these guests will come to our next dinner as honoured members instead of as honoured guests.

Gentlemen, I have much pleasure in giving you the toast of "Our Guests," coupled with the name of Mr. Geoffrey Evans.

Mr. Geoffrey Evans, C.I.E., in responding to the toast of "Our Guests," said: During the course of my career, I have, however, occasionally come across Petroleum Technologists. My first introduction to them was at a rather unattractive place called Abadan, at the head of the Persian Gulf. I never could make out why it was given this name, because every white man appeared to be a Scotsman, and even the local inhabitant, who spoke a mixture of Arabic and Persian, did so with a strong Scottish accent. I think there must have been a mistake somewhere in the past, and that it should have been called Aberdeen and not Abadan. Well, to be perfectly candid, as members of the Expeditionary Force "D," we were all rather suspicious about the Petroleum Technologist, because every man was firmly convinced that if some clever Petroleum Technologist had not discovered oil in the place there would have been no pipe-line from Abadan to Dhar-i-Khazineh and no necessity for the Expeditionary Force, so that, before I was transferred to Trinidad, I naturally looked upon Petroleum Technologists with a certain amount of suspicion, for Mesopotamia was not a pleasant place to campaign in. However, contact with them here in their natural habitat has removed all traces of suspicion, and I have found out what a useful asset they can be to a colony.

Speaking as an agriculturist, I would like to point out some of the ways in which the oil industry is of direct interest and value to an agriculturist. I think you will agree with me that many a poor cocoa planter in Trinidad, who has been struggling with adversity for many years faced with poor prices, with broom, black pod and *Steirostoma depressum*, blessed the day when the first Petroleum Technologist came to Trinidad. He is now living in affluence in Port of Spain, and has leisure to attend all the meetings of the Agricultural Society, and to give his less fortunate brethren all his experiences and the benefits of his advice.

As a scientist—I must not speak as an agriculturist now—there is one point about the work of the Petroleum Technologist that appeals to me very strongly, and that is their efficiency. There is no doubt the industry is highly efficient. Ordinary mortals like myself have only to travel down the Southern Main Road and pass Pointe-a-Pierre to know that an industry that can produce such an aroma from its cracking plant cannot be anything else but super-efficient. Seriously speaking, however, gentlemen, there is one point about the oil industry that has interested me, and it is that Trinidad originally was primarily an agricultural colony. It was formerly dependent upon agricultural products. It is the

only British colony in the Caribbean which has another major industry besides agriculture, and you have only to look at this colony and see its prosperity as compared with other colonies that have no oil industry to rely upon.

We are passing through a period of depression, and previous speakers have enlarged upon the point. Everyone hopes that the depression will pass, and that the oil industry will again get into its stride. Speaking as an agriculturist, I sincerely hope that the expansion will not come too rapidly, because if you start exploiting the oil resources in Trinidad too quickly, the results will have an adverse effect on agriculture. In the first place, it is unwise to draw on the labour supply too rapidly. If you develop the oil resources too quickly, you will attract a great deal of labour from agriculture, and, in the course of comparatively few years, it is possible that you may remove most of the oil reserves, and then Trinidad will be left in a most unfortunate position, having a large industrial population which cannot be fully employed. I hope, therefore, that the development of the oil reserves of Trinidad, from the point of view of agriculture, will not be too rapid, but will be developed wisely and having regard to the labour available for agriculture.

I am certain that I can say one thing on behalf of the guests, and that is, we have the greatest admiration for the Petroleum Technologist and the Institution as a whole. We wish the Institution every success, and trust it will continue in its efforts to develop the oil industry of Trinidad. I have pleasure in responding for the guests and in thanking the members present for their hospitality.

Lubrication Congress, Strasbourg, July 20th-26th, 1931.

By A. Graetz.

This Congress was organised by the "Office National des Combustibles Liquides" and by the "Ecole Superieure du Petrole" of Strasbourg, and represented the collaboration of the "Chambre Syndicale des Importateurs d'Huiles de Graissage," the "Syndicale d'application des Combustibles Liquides," the "Compagnie Française de Raffinage," the "Société d'Exploitation Minière de Pechelbronn," and other interested companies.

More than 50 papers were contributed, and the sessions were attended by many delegates and were productive of a useful interchange of ideas.

The papers presented may be classified into four groups as follows: Constitution, Analysis, Refining and Uses.

Constitution of Lubricants.—Professor Kugel, of the "Ecole du Petrole" of Strasbourg, presented a particularly important paper on the relation existing between the constitution of hydrocarbons of high molecular weight and their viscosity.

M. Kugel prepared a whole series of lubricants from oils obtained by hydrogenation of pitch from high temperature coal-tar (polycyclic hydroaromatic hydrocarbons derived from anthracene, naphthanthracene, pyrene, chrysene and picene). He introduced into these complex molecules, side chains—benzyl, isoamyl, isohexyl, di-isoamyl, hexadecyl. In this way he obtained a whole series of different compounds of known constitution.

From a study of the viscosities of these compounds the following conclusions can be drawn.

The production of closed rings increases the viscosity to a remarkable extent. Cyclic bodies with 10 carbon atoms have properties very similar to those of the solid paraffins. From the point of view of increase in viscosity, the cyclo-pentane and cyclo-hexane rings are the most interesting.

Acyclic side chains have comparatively little influence on viscosity. The introduction of methyl groups into cyclic compounds of high molecular weight, considerably increases the viscosity.

The presence of double bonds in acyclic chains has very little influence on the viscosity, but saturation increases the viscosity of cyclic hydrocarbons.

In general, it appears that the presence of a central group giving the viscosity is necessary. This group may be a ring but it can also be a carbonyl carbon atom.

Finally, from viscosity/temperature curves, it seems that the higher the molecular weight of a lubricant (at equal viscosities), the better will be the viscosity curve.

Analysis and Examination of Lubricants.—Among the papers dealing with this section some deal with the study of the viscosity of lubricants, while others are more particularly concerned with the sources of error and improvements in measuring various physical or physico-chemical constants of a lubricant. Finally, methods of artificially ageing oils have been specially studied with a view to obtaining more knowledge of the changes occurring in oils.

Viscosity.—MM. Woog and Louis recommend the direct measurement of absolute viscosity in the laboratory.

M. Weich considers that only the empirical viscometers are of practical value.

Messrs. Garner and Kelly bring forward a suggestion which allows the use of the empirical apparatus but expresses the results in absolute units.

They propose formulæ and tables for the conversions between kinematic viscosity units and times of flow in the various commercial viscometers.

Messrs. Garner and Kelly have endeavoured to obtain the constants of a Redwood No. 1 Viscometer, which conforms in all its dimensions to the specifications of the Institution of Petroleum Technologists (1929). They propose two equations for the conversion of times of flow to kinematic viscosities :—

$$V = 0{\cdot}00255\ T - \frac{2{\cdot}0}{T} \quad \text{for } R_1 \text{ from 34 to 110 secs.}$$

$$V = 0{\cdot}002435\ T - \frac{0{\cdot}6}{T} \quad \text{for } R_1 \text{ above 110 secs.}$$

For Redwood No. 2.

$$V = 0{\cdot}02458\ T - \frac{1{\cdot}0}{T} \quad \text{for } R_2 \text{ between 32·5 and 90 secs.}$$

$$V = 0{\cdot}02447\ T \quad \text{for } R_2 \text{ between 90 and 250 secs.}$$

For Saybolt Universal.

$$V = 0{\cdot}00226\ T - \frac{1{\cdot}95}{T} \quad \text{for } S_u \text{ between 32 and 145 secs.}$$

$$V = 0{\cdot}00220\ T - \frac{0{\cdot}8}{T} \quad \text{for } S_u \text{ above 145 secs.}$$

For Saybolt Furol.

$$V=0{\cdot}0224\ \ T-\frac{1{\cdot}84}{T} \text{ for } S_f \text{ between 25 and 40 secs.}$$

$$V=0{\cdot}0216\ \ T-\frac{0{\cdot}6}{T} \text{ for } S_f \text{ above 40 secs.}$$

For Engler.

$$V=0{\cdot}08E^\circ-\frac{0{\cdot}0864}{E^\circ} \text{ for } E^\circ \text{ between 1·35 and 3·2° E.}$$

$$V=0{\cdot}076E^\circ-\frac{0{\cdot}04}{E^\circ} \text{ for } E^\circ \text{ above 3·2.}$$

Messrs. SOUTHCOMBE and WELLS have devised a machine to study imperfect lubrication and oiliness, which is simpler than other apparatus designed to study surface phenomena.

The feature of this apparatus, which cannot be described here, consists in the fact that the friction surfaces are maintained constantly parallel during the operation in spite of the vibrations of the motor. This favours the state of imperfect lubrication.

By means of this apparatus the authors have studied the influence of the materials composing the friction surfaces—the lubricant, the speed, the pressure, the temperature, etc.

They have observed that lubrication is favoured by the addition of oleic acid to a mineral oil. Similarly they have shown that the co-efficient of friction for a given oil was less at high pressures than at low pressures. An addition of 0·8 per cent. oleic acid lowers the co-efficient of friction in both cases, but the decrease is greater than at high pressures.

Finally the authors suggest the existence of a primary and a secondary film in perfect friction. The primary becomes the secondary and vice versa according to the speed and load. In consequence of the decrease in speed or increase of load, the film is replaced by a kind of plastic film and the co-efficient of friction increases to about 100 times its original value.

Mr. WINSLOW HERSCHELL, Chief Assistant of the Bureau of Standards (Washington, U.S.A.), explained the researches on lubrication carried out by the American Society of Mechanical Engineers. The Committee of Mechanical Engineers, appointed in 1915, collected a complete bibliography on all matters concerning lubrication, and acts as liaison medium between American and Foreign laboratories which are occupied with the same questions. It compares, also, the results obtained with those of its own researches and co-ordinates the conclusions.

For the moment, the activity of the committee is concentrated on three problems :—

1. A study of viscosity under pressure.
2. Research on lubrication of bearings and journals.
3. Research on lubricating qualities.

Researches on viscosity under high pressures have already shown that a complete understanding of the properties of lubricants can be obtained only by considering the absolute viscosity as a function of the pressure and temperature at the time, and that a solidification effect is produced with increasing pressures at constant temperature which must bear a relation to oiliness.

Dr. TAUSZ (Karlsruhe) showed that lubricating oils can be distinguished by studying changes in viscosity of solutions of the oil in certain reference solvents.

The author favours the use of toluene as reference solvent to obtain quantitative mixtures. He has determined the exponential function of the undiluted oil according to the expression :—

$$n^x \text{ (undiluted)} = n \text{ (diluted)}.$$

A study of a whole series of diluted oils in 10 or 20 per cent. solution in toluene has given some interesting observations.

The greatest values of " x " have been observed for vegetable oils and fatty acids ; then come naphthenic and aromatic oils.

It appears that the greater the value of " x " for any oil—the better will be its lubricating properties.

Distillation under Cathode Vacuum.—Distillation under cathode vacuum has been proposed by M.M. Weiss, Louis, Iselin and Schmeleivsky of the " Ecole du Petrole," of Strasbourg, as a means of determining the different fractions in a crude petroleum, and also as a method of investigating lubricating fractions.

M. LOUIS outlined the modifications introduced into the apparatus to facilitate its use. Particularly better results have been obtained by suppressing bubbling by hydrogen. Interesting results have been obtained on the constitution of oils. On the same product the figures obtained are constant. This method, in conjunction with another method of physical fractionation, is capable of giving interesting information.

It is already used in practice. Professor WOOG described the apparatus for distillation under vacuum used in the laboratories of the " Compagnie Française de Raffinage."

The Estimation of Sulphur in Light Factions of Petroleum has been studied by MM. Boiselet and Koyloff, who bring forward a method which consists in oxidising the sulphur compounds contained

in a fraction of the petroleum by the action of the products of electrolysis of nitric acid.

This method requires no attention and gives good results for bodies such as thiophenes, mercaptans, sulphides and disulphides. When the amount of sulphur in the sample is very high, it is necessary to dilute in liquid paraffin.

The Acidity of Lubricating Oils can be obtained by potentiometric titration using the antimony electrode of M. Vellinger. This titration gives a neutralisation curve analogous to those obtained in aqueous solution. The point of inflexion of the neutralisation curve has a different value according to the nature of the acid. This feature allows an accurate distinction to be made between mineral and organic acidity.

M. TERPOUGOFF outlined a method for titrating the acidity in the presence of absolute alcohol.

The Degree of Refining of a Lubricating Fraction can be determined by studying the interfacial tension between its fractions and aqueous solutions of electrolytes (also described by MM. Weiss, Vellinger and Radulesco).

The interfacial tension of crude distillates treated with absorbent earths rises rapidly as a function of the amount of earth used.

This increase in interfacial tension is always accompanied by an appreciable decolouration of the treated fraction.

Freezing.—M. TERPOUGOFF points out that the freezing point of mixtures of lubricants prepared by heating is usually greater when determined immediately after cooling than when the determination is made after several days. He has encountered only one case in which the reverse occurred.

DR. ESK, of the "Physikalisch Technische Reichsanstalt" (Berlin), sought to determine and to co-ordinate methods of analysis of oils, particularly the determination of Pour Point (A.S.T.M.), Pour Point (Deutscher Verband für die Material Prüfungen der Technik), the degree of fluidity (Deutsche Reichsbahn), viscosity by various capillary viscometers (diminishing progressively the temperature until the unit of flow is obtained), the paraffin content (by precipitation). There is no relation between the results obtained by different methods. But the determination of the solidification point in conjunction with measuring the viscosity can lead to interesting results.

Determination of Carbon Residue.—Mr. KELLY (Anglo-American Oil Co.) described the Ramsbottom method (Royal Aeronautical Establishment, Farnborough) adopted as standard by the Institution of Petroleum Technologists. This method for determining

carbon residue is practically free from the personal error; it is useful for determining the relative efficiencies of absorbent earths in the treatment of filtered cylinder oils, and to estimate the tendency of any lubricating oil to form carbon deposits in engines.

The Colour of Lubricating Oils can form an interesting indication of their degree of refining. In conjunction with the viscosity and flash point, M. Herbrich considers that colour can be equally as important as the Conradson test.

A method is outlined which uses the colorimeters of Lovibond and Dubosq.

Exhaustive studies have been devoted to methods of artificially ageing lubricating oils, methods which allow an oil to be evaluated under conditions approximating to those occurring in practice. It appears that these determinations will be commonly used in the near future—if they have not already been adopted in a certain number of laboratories.

M. VELLINGER (Ecole Superieure des Petroles) suggests that the superficial activity of oils, measured by the contamination effect on clean surfaces, taken in conjunction with the lowering of the corresponding interfacial tension, can be used to study the alteration occurring in oils. This alteration is shown also by certain modifications in spectrum.

M. VAN RYSELBERGHE (Brussels) studied the resistance offered to oxidation by lubricating oils. He examined the effect of various factors—particularly the catalytic influence of metals. Experiments made at the "Service Technique de l'Aeronautique Française" show that the deposits which occur in the hottest parts of engines have a high oxygen content.

Much work has been devoted to a study of ageing, this will be referred to again in the paragraphs dealing with turbine oils, transformer oils and superheated oils.

Standardization of Methods of Analysis of Lubricants.—The "Chambre Syndicale des Importateurs d'Huiles de Graissage" presented a scheme of standardization established in collaboration with the engineers of the lubrication companies and on the recommendation of Professors Weiss and Woog of the "Ecole du Petrole" of Strasbourg.

The object of this scheme was to do away with certain tests which were useless or where their use led to confusion and gave a false idea of the oil under examination.

(Particularly the soda test, the sulphuric acid thermal test, the acid tar number, the iodine value of mineral oils, etc.)

The methods retained have been divided into three groups :—

Standards.—Methods in common use, their employment being general because they have been found to be quite satisfactory.

Tentative.—Methods which it would be interesting to adopt but which have not been accepted in general practice.

Provisional.—Imperfect methods, but which cannot be dropped for want of something better to take their place.

PHYSICAL TESTS.

Once the physical constants have been scientifically defined, and the units in which they must be expressed have been fixed in some definite system, then they can be determined by any apparatus embodying correct physical principles.

Viscosity.—Expressed in absolute units : Baume Vigneron, Ubbelhode, B.E.S.A., Vogel, Ossag, Engler, Barbey (provisional).

Freezing Point.—A.S.T.M. (provisional).

Pour Point.—" Compagnie Française de Raffinage " (Tentative).

Solidification Point of Paraffin.—A.S.T.M. (Standard).

Drop Point of Greases.—Ubbelhode-Richtlinien (Standard).

Softening Point of Pitch.—A.S.T.M. (Ring and Ball) (Standard).

Closed Flash Point.—Luchaine (Standard).

Open Flash and Fire Point.—Cleveland (Standard).

Colour.—Dubosq colorimeter (Tentative).

CHEMICAL TESTS.

Acidity, Alkalinity, Ash, Saponification.—(Standard.)

The following methods have also been accepted as standards :—

Sediment Content.—Extraction with benzene.

Water Content.—Xylene method.

Hard Asphalt Content.—By Petroleum Ether (B.Pt. 35-50° C.—S.G. 0·640—0·655).

Sulphur.—Bomb.

Unsaponifiable Matter.—Standard method for fatty materials.

TRANSFORMATION TESTS.

Deterioration of Transformer Oils.—Weiss and Salomon method (Tentative).

Coke Residue.—Conradson (Provisional).

Demulsification.—Herschell.

After this report it was decided to appoint a permanent Standardization Committee which will form the basis for an International Standardisation Committee for petroleum products. This committee will work in close touch with the standardization organisations in the various countries.

Preparation of Lubricants.—M. SCHMITZ described the process of neutralisation of crude petroleum and its derivatives, and pointed out the advantages in certain cases of a preliminary neutralisation of crude petroleum. Various papers were also presented dealing with the use of the centrifuge in refining.

USE OF LUBRICANTS.

Transformer Oils.—The "Société La Mailleraye" has studied the alteration in transformer oils during storing. Deposits have been found, and it is apparent that in most cases the deterioration varies with the time of storage. It increases for several days following the manufacture of the oil in the refinery, then it diminishes and the deterioration curve tends to approach the initial curve.

M. FLAMANC made known the existence of an optimum point of sulphuric refining as a function of the stability of transformer oils.

Superheated Oils.—M. Boissilet (Professor at the "Ecole du Petrole," of Strasbourg) studied the action of steam on lubricating oil by means of an apparatus of his invention. It seems that up to 300° C., the oil does not alter appreciably in contact with steam. Above 310° C. the increase in viscosity is rapid. The conversion to pitch occurs towards 400° C.

Turbine Oils.—M. BOHNENBLUST described the methods for controlling turbine oils, adopted in the laboratories of Brown-Boveri. An ageing experiment is first carried out, then demulsification with a jet of steam. A graphical method, perfected by the company, enables comparable results to be obtained.

M. SALOMON, of the "Ecole du Petrole," of Strasbourg, described the mechanism of the changes in oils used in steam turbines—it approximates to that occurring in transformer oils. The method of artificially ageing advanced by Weiss and himself is also described, and it appears that there is a close relation between the tendency to form emulsions and the tendency to form deposits. Finally, M. Bressaud studied the influence of water mixed with the lubricating oil on the operation of steam turbines (the formation of emulsions, attack on metals, formation of deposits, seizing, etc.).

Aircraft Engines.—M. Champsaur, Chief Engineer of the "Aeronautique Française," presented an interesting paper on the amount of heat withdrawn by the oil in aviation engines; this quantity can give important information as to the working of the engine and its adjustment. The heat withdrawn by the oil increases with the supply of oil and also as the amount of heat removed by the water diminishes.

Apart from its function as a lubricant, therefore, the oil can act as a cooling agent.

M. Champsaur varied the temperature of the water and observed that, at lower temperatures, the amount of heat absorbed by the water diminished, but this was balanced by an increase in the heat absorbed by the oil.

If the temperature of the oil is varied, then the amount of heat absorbed by the water remains practically constant. The power increases as a result of the decrease in viscosity, and the amount of heat withdrawn by the oil diminishes.

Vegetable Oils.—M. André described his researches on the constitution of castor oil which contains:—

A steam-diricinolein.
A dioleo-ricinolein.
A linoleo-diricinolein.
Some tri-ricinolein.
A diricinoleo-monodioxy stearin.

M. André, by selective exhaustion of the castor oil, has been able to separate the various constituents and obtain oils of different viscosities, some of which are particularly suitable for use as lubricants and mix well with mineral oils.

In a general survey of recent tendencies, as revealed by the Congress, it appears, first of all, that the old types of viscometers are being more and more replaced by apparatus, by which absolute kinematic viscosity can be measured. At present we are at the intermediate stage, and it is not possible suddenly to replace all existing apparatus. Nevertheless, a great effort has been made to adopt absolute viscosity as a standard. M. Woog described the apparatus installed and in daily use in the laboratory of the "Compagnie Française de Raffinage." Nothing could be more simple or easy to manipulate.

A second point of note is the attempt to standardise methods of analysis. This is a most desirable object requiring the collaboration of all, and it will result in a great simplification of work and a better understanding of the interpretation of results.

A third point is the great progress made in the study of the relation existing between the constitution of an oil and its lubricating properties. On this subject the work of Profs. Tausz and Hugel is worthy of note.

Finally, attempts to reproduce in the laboratories the working conditions of the lubricant are being more and more adopted. There is no doubt that methods of artificial ageing of lubricants will give results much more interesting than many of the laboratory tests which are not based on an exact knowledge of the conditions under which lubricants are used.

BOOKS RECEIVED

LUBRICATING OIL TESTS AND THEIR SIGNIFICANCE. J. E. Southcombe. Pp. 69. London: Henry Wells Oil Co., Ltd. 2s. 6d.

For the user of oil and for the oil salesman the major portion of the literature on lubricants is too highly technical to be of any useful service. In this book Mr. Southcombe has contrived to present much information regarding lubrication and lubricants in such a way that it can be readily assimilated by the non-technical man, although the technical man will find much to interest him. As the title suggests, the book is chiefly concerned with a description of the tests and their indications, but there are also chapters on lubrication principles and on the behaviour of lubricants.

INDEX TO A.S.T.M. STANDARDS AND TENTATIVE STANDARDS. September, 1931.

The 1931 Index to the Standards and Tentative Standards of the American Society for Testing Materials is of value not only to those who are familiar with these Standards, but also to those who are not. The index covers the 443 standards and 180 tentative standards issued by the Society, and forms a very convenient and ready means of ascertaining whether any standards on a specific subject have been issued and where such standards are to be found. Copies are furnished free of charge to those interested on application to the Society Headquarters, 1315, Spruce Street, Philadelphia, Pa., U.S.A.